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A

TEXT-BOOK OF CHEMISTRY.

INTENDED FOR THE USE OF PHARMACEUTICAL
AND MEDICAL STUDENTS.

BY

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PREFACE.

An experience of some seventeen years as teachers in a professional school, where Chemistry is considered one of the foundation-stones upon which young men must build a technical education, has convinced the authors that the subject must be taught in a way that, while thoroughly scientific, is yet distinctly adapted to the ultimate uses of the students.

The professions of Pharmacy and Medicine are closely related, and their uses for Chemistry are very much alike. The members of these professions must understand the composition and chemical properties and possibilities of the whole *materia medica*, both inorganic and organic, in order safely to maintain the important trusts committed to them,—trusts involving the continued health and life of their fellow-men. The importance of thorough chemical knowledge for these related professions is now recognized in the fullest way in their official publication, the U. S. Pharmacopœia, the last edition of which has embodied throughout the most detailed and exact statements of the chemical nature, properties, and reactions of medicinal substances, together with methods of analysis or assay and tests for purity.

We have sought in the following pages to offer a text-book on Chemistry which should combine scientific accuracy and completeness with that special reference to the needs of the pharmaceutical and medical student, as well as those in active professional practice, which will make it of value for both study and reference. Compounds recognized in the U. S. Pharmacopœia are specially indicated, but they are not taken out of their proper position for such discussion.

A brief outline of Elementary Physics, much of which is absolutely essential for the understanding of chemical methods, forms Part I. The convenient division of the elements into Non-Metals and Metals is followed in the main in Parts II. and III., to the limitations made necessary by the chemical relatior indicated by the valence groups. Part IV. deals with (Chemistry. While the arrangement here followed is scientific, it has been sought to give the subject a distinct tical bearing, and to this end the industrial applications ganic compounds have been noted, and in a number (illustrated.

In Part V. a brief outline of Qualitative and Quan Analysis is given, the methods being such as have of value in our own practice. A number of the Phar tical Assays of the U. S. Pharmacopœia are also added.

The Appendix contains, besides a list of the chemical el with atomic weights and valences, thermometric scales a specific gravity tables in most general use.

The authors have made free use of many chemical work as Flückiger's "Pharmaceutische Chemie," Schmidt's "P ceutische Chemie," Meyer and Jacobson's "Organische Ch Bernthsen's "Organische Chemie," Weyl's "Organisch mie für Mediciner," Fischer's "Neuere Arzneimittel," Ga "Physiological Chemistry," Pictet's "Alcaloides Végé Power's "Essential Oils," Allen's "Commercial Organic ysis," Prescott's "Organic Analysis," and Sadtler's "Ind Organic Chemistry."

Our thanks are due to J. C. Peacock for valuable assista the preparation of Parts III. and V., to S. S. Sadtler a Blount Hunter for work on the index, and to Edwin T for the execution of many original drawings for the illust of the work.

S. P
H. T

PHILADELPHIA, February, 1895.

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PART I.

ELEMENTARY PHYSICS.

PART I.

ELEMENTARY PHYSICS.

CHAPTER I.

MATTER, FORCE, AND MOTION.

1. Introductory.

Science is the attempt to classify facts or observations according to apparent points of resemblance or difference and to suggest underlying causes for these.

Matter is that which occupies space and is apprehended by the aid of our senses.

Physical Sciences.—All branches of physical science, as opposed to metaphysical science, are concerned with the study of matter, its properties, forms, motions, and the laws which determine and regulate these. We may again distinguish between the descriptive or natural history sciences, such as *mineralogy* and *geology*, *botany* and *zoölogy*, which are chiefly concerned with the outward forms and appearance of matter, and the exact physical sciences, such as *chemistry* and *physics*, which are concerned with the internal composition of matter and the motions of which it is capable.

Relationship of Physics and Chemistry.—It is obvious that, while the range of phenomena covered by physics and chemistry is a very wide one, the relation of the two branches is very close, that they are mutually dependent one upon the other, and that a clear understanding of the results of the one science involves at least a knowledge of the generalizations of the other and a summary of its results. An outline of those branches of physics which bear most closely upon chemical phenomena should, therefore, precede the detailed study of the latter science.

2. General Definitions.

Extension.—Matter has already been spoken of as occupying space. It therefore has **extension**, and this conception of it necessarily results from the fact that its existence is made evident by our senses, whether immediately, as by the aid of sight or touch, or more indirectly by the aid of the senses of hearing, smelling or tasting.

Divisibility.—If matter have extension, we must also admit its divisibility. That most forms of matter about us can be divided into smaller fragments or portions is a matter of every-day experience. We break a stone or piece of rock into fine fragments. These can then be ground to still finer powder, and so the subdivision carried on. There is, of course, a practical limit to this because of the coarseness of the tools with which we work. Under a powerful microscope the finest solid particles obtained by grinding or the minutest film of liquid, show plainly the possibility of further subdivision.

Molecules and Atoms.—The smallest particles of matter which we can conceive of as obtained by this mechanical or physical subdivision we call *molecules.* How large these molecules are, what their shape is or what their absolute weight is, we do not know. We merely know that they still show the distinctive properties which pertained to the masses of matter with which we started and that therefore physical or mechanical means have not been able to tell us anything of the composition of the material in question. But many of these forms of matter, although not capable of resolution into anything different by methods of mechanical subdivision, are capable of decomposition into simpler forms under the influence of chemical reagents. We assume, then, that molecules are made up of still smaller particles, to which the name *atoms* has been given. These smallest particles of matter are supposed to be unalterable.

Simple and Compound Matter.—The union of like atoms gives us simple or elementary matter of which chemists have distinguished some seventy kinds, while the union of unlike atoms gives us compound matter, the varieties of which are almost endless.

Indestructibility of Matter.—If, as stated, the atoms or smallest conceivable portions of matter are final unalterable particles, it follows that matter is indestructible whatever be the influences to which it may be subjected and the changes of form which it may undergo. Compound matter may indeed be resolved into simpler combinations and ultimately into elementary matter, under the influence of chemical treatment, but the sum total of the products so obtained must always equal that of the matter operated upon. Cases of apparent loss or destruction of matter are all explained upon careful examination of the reaction in its several phases. Changes of outward form take place under the influence of physical agencies alone, so that a solid or liquid may lose in weight by the escape of a gas or vapor, and changes in the method of combinations of the atoms may take place under the influence of chemical reagents, but if the products are examined it will be found that no new atom has been created nor has any been destroyed.

Solid, Liquid, and Gaseous States.—Changes in the appearance of matter do not necessarily imply a change in the composition of the material examined or in its essential properties. The change may be merely in the aggregation of the molecules constituting it. We recognize three states of aggregation in matter,—the solid, the liquid, and the gaseous. In the first of these the molecules are held firmly together, so that the mass of matter tends to retain its shape, and the exertion of some force is necessary to overcome the adhesion of the molecules and change the shape ; in the second, the molecules move easily past each other and the liquid readily assumes the shape of the containing vessel ; in the third, the molecules are tending to separate, and the gas, consequently, is tending to expand in volume, pressure being required to overcome this tendency.

Physical and Chemical Changes.—The same body may, under certain physical influences, such as the action of heat, assume one after the other of these conditions in succession. Thus, a piece of ice under the influence of heat may melt, and so pass into the liquid state, when it is known as water, and at a still higher temperature may assume the gaseous form under the name of steam. It remains one and the same substance, however, through these successive changes. The withdrawal of the heat, or the action of cooling agents, will cause the vapor to condense to a liquid, and the liquid in turn to become a solid, which when examined proves to be identical in properties, physical and chemical, with that from which the liquid and vapor were originally formed. Such a change is obviously a temporary one, dependent upon the conditions of temperature existing at the time, and is known as a *physical* change, as it does not affect in any way the chemical composition of the body experimented upon. If, however, the water, instead of being simply heated, is submitted to the action of an electric current, it is changed, and two gases, known as hydrogen and oxygen, are given off and can be collected. Upon the withdrawal of the current these do not reunite to original liquid. The water has been decomposed, or ha gone permanent alteration which is characterized as a change.

It is obvious that only changes of the latter class a composition of a molecule. Under the influence of forces alone the molecules may be given a variety of the manifestations of which are known to us under the names of heat, light, magnetism, electricity, etc., but the i of the molecule is still preserved. We know nothing nature of the matter so affected, whether it be elemen compound. This question is solved only when the mol broken up and its constituent atoms are rearranged un influence of chemical change, or, as it is generally c chemical reaction.

3. General Properties of Matter.

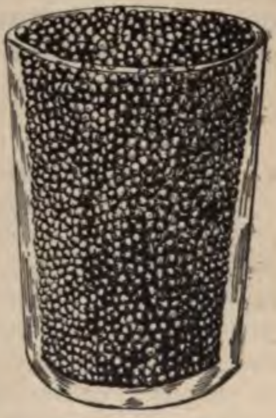
Extension and divisibility have already been referre self-evident from our conception of the existence of ma demonstrated to us by the aid of our senses. We are led use of these senses to ascertain length, breadth, and thick material objects, and thus arrive at the necessity for u measurement (see p. 19). It matters not that an object extremely minute, so that it is perceptible only by the powerful magnifying apparatus; so long as we grant its exis even as a single molecule (see p. 14) we must conceive c possessing definite shape or form, and hence extension.

The actual size of molecules has never been determin measurement, but physicists have endeavored to make ap mate estimates. According to Sir William Thomson, " conceive a sphere of water of the size of a pea to be mag to the size of the earth, each molecule being magnified t same extent, the magnified structure would be more coarse gr than a heap of small lead shot, but less coarse grained t heap of cricket-balls."

The testimony of our senses bears just as strongly witness to t property of divisibility. This is illustrated best by the st microscopical objects. Some of the most minute of living organisms that have been distinguished nevertheless have a rela tively complicated structure and show different organs for as similation of food, the ultimate particles of which must be [illegible] small. The very thin films of metal, like gold leaf, s that may be deposited on glass are also illustrations of the divisibility of matter. They show distinctly the metallic lustre and color, yet are so thin that light shines readily through them.

Impenetrability is also an essential property of matter. As matter occupies space, we believe that any particular space cannot be occupied by two different bodies at the same time. Thus, if a solid body, like a bar of metal, be immersed in a tumbler previously filled with water, it will cause some water to overflow. The amount so displaced will exactly equal the volume of the solid immersed. Numerous apparent exceptions to this rule exist, as when a nail is driven into a piece of wood, or water is poured into a tumbler previously filled with dry sand, or a piece of dry wood is dipped into water. But in all such cases we must take account of another property of matter, viz., *porosity*. In the use of this term we mean that the molecules of a substance are never in actual contact, but are separated by spaces relatively large as compared with the size of the molecules themselves. These spaces are called *pores*, and their existence is made evident when pressure is applied and the mass is diminished in bulk. This diminution in the space occupied under increase of pressure shows most notably with gases, which are therefore termed the most compressible, but occurs also in liquids and solids. This is explainable only by the assumption of the porosity of matter. A clear illustration of this is had when we mix equal volumes of alcohol and water. Instead of the mixture equalling the sum of the two liquids, it is only about ninety-five per cent. of the combined volume. The structure of some solids is such that open spaces, termed sensible pores, show in their mass, as in the case of most woods, sponges, unglazed brick, filter-paper, etc.

FIG. 1.



Porosity.

Porosity is well illustrated by the tumbler filled with shot, shown in Fig. 1. It is obviously possible, after filling the tumbler with the shot, to add quite an amount of a liquid which shall fill up the spaces between the shot without overflowing the tumbler.

Connected with and dependent upon the porosity of bodies is the property of *compressibility*. As before stated, gases are the most compressible of bodies. In them the molecul widely separated than in liquids or solids, and are separate still more widely; but for this very reason th more readily to the influence of pressure and can be into smaller space. As we will see later, temperatur pressure has much to do with this change of volume.

The compressibility of liquids is but slight, but, noted in the case of the mixture of alcohol and wate shown to exist. Solids, on the other hand, may be pressible, the change in this case depending, howev upon the existence of sensible pores, as in the case cork, paper, etc., which readily yield to pressure. also compressible, as is shown in the process of stam with hardened dies.

Elasticity is the property by virtue of which bodies undergone compression tend to resume their origin volume upon the removal of the compressing force. It goes hand in hand with the property of compressibility which are the most compressible of the several forms are also the most elastic. Liquids in the degree that compressible under pressure are also perfectly elastic show the property of elasticity in varying degrees. In existence of sensible pores allows a body to show a hig of compressibility without a corresponding elasticity, a solids which are elastic after moderate compression sho of elasticity, and when this is passed do not readily resu original form or volume.

Mobility and inertia, which are general properties dependent upon motion, will be referred to later (p. 20).

4. Volume and Mass.

Volume. As before stated, our most elementary co of matter is that it occupies space. The amount of space pies is termed its volume. We can conceive of its exte one direction only, which we call space of one dimen length; of extension in two directions, which we call two dimensions, or area; of extension in three direction we call space of three dimensions, or volume.

Mass means quantity, and as matter occupies space have a definite quantity or mass. This may o[illegible] a l smaller volume, according as its molecules are [illegible] or l rated from each other, or according to what is termed its

Mass, therefore, represents the product of the volume by the density, or, as it is expressed, $M = V \times D$.

Unit of Length.—The English unit, still in common use, is the foot, with its subdivision, the inch, and its multiple, the yard; the French unit, used universally in scientific calculations, is the meter, with its decimal subdivisions, the decimeter, centimeter, and millimeter.

Unit of Area.—The English units are the square inch, the square foot, and the square yard; the French units, the square meter, the square decimeter, and the square centimeter.

Unit of Volume.—The English units, the cubic inch and the cubic foot, are not in general use. Various units are used, as the pint, quart, and gallon for liquids, and the peck and bushel for solids. The French units are the cubic decimeter, or the liter, and the cubic centimeter.

Unit of Mass.—The English unit is the pound avoirdupois, which bears no simple relation to the units of volume; in the French system the unit is the mass of a cubic centimeter of distilled water at the temperature of its maximum density (4° C.). This is the gramme, and its multiples and submultiples are all decimal.

It is obvious that the French or metric units are simpler and more easily connected with each other than the English units still in common use. It is to be hoped that the metric system will, at an early day, be adopted in England and the United States, as it has been accepted elsewhere throughout the world, and especially in all scientific usage. Tables of the metric system and of English weights and measures will be found in the Appendix.

5. Motion and Force.

In our statement of the general properties of matter, extension and impenetrability were defined. Both of these conceptions imply a fixed position as assignable at any time to the mass or molecule of matter under consideration. If this position remain constant through a period of time, we speak of the body as at rest; if it is changing, the body is said to be in motion. We must remember that these statements are not to be taken as absolute. The body is at rest with reference to its original position, or in motion with reference to the same, while both the body and the original fixed point may be in motion with reference to some other distant point. Motion and rest are therefore purely relative ter

Inertia, which is one of the fundamental properties of
means that matter itself is not capable of changing the
which may have been imparted to it, either as to dir
velocity, and that, except for other influences, this motio
continue indefinitely. At the same time, because of this
matter cannot begin to move until it responds to the exe
some force. *Mobility* is the property in virtue of which
yields readily to the exertion of some force, causing it to
its relative position, or inducing motion.

The *velocity* of a particle of matter is the rate of its m
any given time.

Force is that which by acting upon matter either prod
arrests motion. It is a manifestation of energy, and
originated in a variety of ways. Thus, we speak of c
forces, which are manifestations of atomic energy; of m
forces, which result from molecular energy; and cosmic
which illustrate the energy of large masses.

Work is energy applied in overcoming resistance, as
man lifts some article from the ground, where the attrac
gravitation is to be overcome, or when an engine pulls
overcoming the resistance due to inertia and friction.

The unit of work is the work done in raising a unit of
through a unit of height. As we have already seen, the
of weight and measure differ in the English and the Frenc
tems, hence different units must be taken according as one
other system is used. The *foot-pound*, or the work do
raising one pound avoirdupois one foot, is the English unit
the *kilogram-meter*, or work done in raising one kilogram
meter, is the French unit. For work with engines, a
unit, the *horse-power*, is taken. This is equivalent to 3
foot-pounds per minute. In determining the amount of
of an engine in terms of horse-power, we multiply the weig
pounds by the height in feet to which it can be raised, divi
the number of minutes and by 33,000.

Energy is capacity for doing work. It is possessed by m
in virtue of its mass and velocity, and its exercise involves m
of some kind. Thus we have the energy of visible motio
the mass and the energy of the invisible motion of the molec
which is known to us under the forms of heat, sound, ra
energy, or light, and electricity.

Energy may be potential or actual. A weight held up b
hand, or by a support, has the power, because of its positio

fall, and thus do work, if the support be withdrawn. This is potential energy, or energy of position. Numerous applications of this suggest themselves, as the case of a wound-up spring, or an elevated tank or reservoir of water. The same weight descending in consequence of the withdrawal of the support, the spring uncoiling, and the water acting upon a turbine wheel, all represent actual energy, or the energy of motion.

Exact measurements have shown us in the cases of the weight, spring, etc., that the actual energy developed exactly equals the potential energy that may have been stored up, and no loss or gain is found when all the elements have been carefully calculated. This principle may, however, be extended not only to all cases of visible energy of motion, but to energy wherever and however manifested. As matter is indestructible, and can be neither created nor destroyed by the changes to which it is subjected, so energy is indestructible, and cannot be created or destroyed. Energy of one form may be changed into energy of another form, but there is no absolute gain or loss in amount. This law is known as the *conservation of energy.*

This change of one form of energy into another without loss of actual amount is one of the most important facts in nature, and one most familiar to us. If we rub the fingers briskly over a surface of cloth or wood, we feel a sensation of warmth. The visible motion of the hand, due to muscular energy, is transformed into that form of molecular energy known as heat. In the steam engine we convert the potential energy of the coal, by combustion, into actual heat energy, and in turn impart visible energy of motion to the piston and connected parts of machinery. This motion, by the aid of a dynamo machine, may be converted into electrical energy, and this in turn into either heat or light energy. This illustrates what is termed the *conservation and correlation of forces*, or, more exactly, *of energy.*

6. Forms of Attraction.

Gravitation.—Every particle of matter is attracted by every other particle. This is due to a form of energy which is universal in its action and operates alike on the largest and the smallest bodies. It is known as *universal gravitation.* The most familiar illustration is the attraction of the earth for bodies upon its surface, known as gravity. Upon this is dependent what is called *weight*[illegible] earth pulls upon every particle of the bodies upon its sur[illegible] in virtue of its superior mass tends to draw them towards its centre. This force is exerted along a straig which, therefore, marks the shortest path towards the centre and is called a plumb-line.

The weight of a body is proportioned to its mass, beca attraction of the earth acts upon each particle which goes t the mass. This mutual attraction diminishes as the bodies from each other, but as the distance from the centre of th to its surface (4000 miles) is so great, compared with the of the body above the surface, the diminution in the we the body at different heights is slight. We express the change in the force of attraction of the earth, or weig saying that the attraction varies inversely as the square distance.

The *unit of weight* is the same as the unit of mass,—one avoirdupois in the English system, and one gramme in the l or metric system.

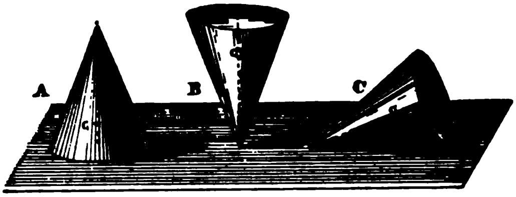
The *centre of gravity* of a body is the point through the line marking the direction of mutual attraction betwe particles of the body and the earth passes. In a sphere c form density this centre of gravity would exactly accor the centre of the mass. In bodies of irregular shape or d it does not so agree.

Equilibrium.—When a body is supported and yet fr swing before coming to rest, it will be in equilibrium wh centre of gravity is in the same vertical line as the point of port. But to insure stability the centre of gravity must al under the point of support and not above it. According t relative position of these two points we have the three cond of equilibrium,—*stable*, *unstable*, and *neutral*. A susp body is in stable equilibrium, therefore, when the centr gravity is below the point of support, in neutral equilibrium they coincide, and in unstable equilibrium when the cent gravity is above the point of support.

Fig. 2 shows us three cones which also illustrate the t conditions respectively. A is in stable equilibrium, the cent gravity being in a straight line below the centre of figure; in unstable equilibrium, as the centre of gravity is above both centres of figure and support: C is in neutral equilibrium, new line between the centre of gravity and point of suppo established whenever it is moved.

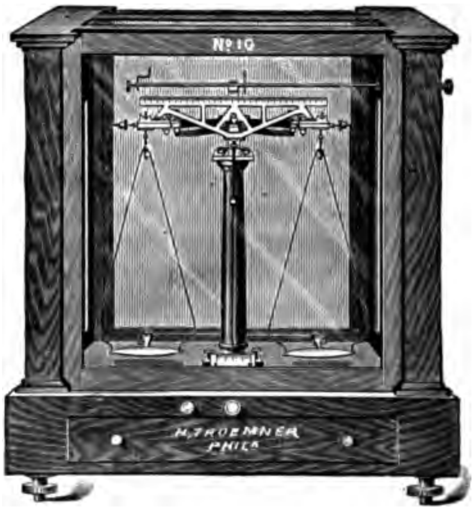
The chemical balance is an important application of the f going principles. As shown in the illustration, Fig. 3, it con of a beam supported in the centre so as to oscillate with the slightest amount of friction. To the ends of the beam are attached supports for the pans, on which the weights and articles to be weighed are placed. By means of a screw adjustment the centre of gravity of the beam can be raised or lowered slightly. The conditions for delicate working of a balance are as follows :

FIG. 2.



Stable, unstable, and neutral equilibrium.

FIG. 3.



Analytical balance.

First, the arms of the balance should be relatively long.

Second, the weight of the beam should be as small as is allowable, while preserving its rigidity.

Third, the centre of gravity should be a little below the point of support.

Molecular Attraction and Repulsion.—Just as the masses of

matter, whether large or small, are influenced by the pow
gravitation, so the molecules which make up the mass are
together with greater or less firmness by the force of mol
attraction. The intensity of this force determines also the p
cal state of the matter concerned. In solids the power of m
ular attraction is most strongly exerted, in liquids it is we
and in gases it seems to be overcome by a force of rep
which tends to separate the molecules.

We distinguish in ordinary usage between the terms *coh*
where molecules of like composition are held together,
particles of iron in a bar of that metal, and *adhesion*,
bodies of unlike composition are held together, as when a
rod is dipped into water, the force of adhesion causes the
to adhere to the solid.

Chemical Attraction.—The attraction between atoms
causes them to unite in the formation of molecules is oth
known as chemical affinity, and will be referred to later.

CHAPTER II.

SPECIAL PROPERTIES OF MATTER.

A. SPECIAL PROPERTIES OF SOLIDS.

IT is obvious from the definition of solids as contrasted with liquids and gases (see p. 15) that they must have properties which are distinctive, and are not shared in any notable degree by the other forms of matter.

Hardness is the resistance to wearing by friction, such as scratching or rubbing, shown by a solid. It is possessed in the highest degree by the diamond, which is, therefore, capable of scratching any other solid.* Hard bodies are often used as polishing powders, as diamond dust, emery, pumice, and tripoli. Great hardness may be imparted to steel and other bodies by a process called tempering, that is, cooling them suddenly from a high temperature. Under these circumstances, however, they usually become more brittle.

Brittleness is inability to withstand compression or a blow, and indicates a want of tenacity or cohesive power between the particles of the solid. It may accompany great hardness, as in the diamond and glass.

Tenacity is the resistance to a tearing or pulling strain exerted upon solids. It may vary in different directions in the same body, as in the case of wood, where it is greater in the direction of the fibres than transversely to them. Closely connected with this are two properties chiefly shown in metals, viz., ductility and malleability.

Ductility is the capability of being drawn out into wires or threads, and is possessed especially by certain metals, like gold, platinum, iron, and copper. Glass and waxes when hot can also be drawn out into fine threads.

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* The hardness of a body is expressed by referring it to a scale of hardness; that usually adopted is, --

1. Talc.
2. Rock-salt.
3. Calc-spar.
4. Fluor-spar.
5. Apatite.
6. Felspar.
7. Quartz.
8. Topaz.
9. Corundum.
10. Diamond.

Malleability is the property in virtue of which bodies are flattened into thin sheets or films under the influence of hammering or rolling. It is possessed especially by metals, such as gold and copper.

Elasticity has already been spoken of as a general property of matter (Art. 10) shared by solids, liquids, and gases, although in unequal degrees. The elasticity there referred to was, however, the elasticity of compression, and was regarded as the complement of the general property of compressibility. Elasticity of tension, or that developed by a stretching force, elasticity of torsion, or that developed by a twisting force, and elasticity of flexure, or that developed by a bending force or weight, are other phases of elasticity peculiarly belonging to solids. A familiar application of the elasticity of torsion is the torsion balance now used extensively in practice, and of the elasticity of flexure, steel springs in watches, carriage springs, etc.

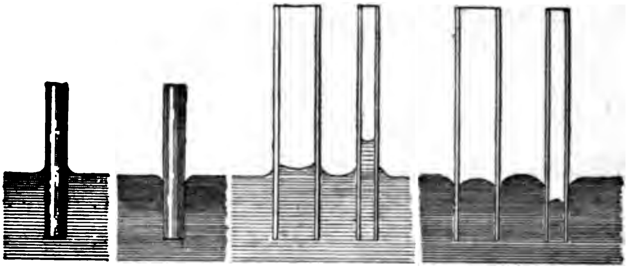
Structure of Solids. A solid is distinguished from a liquid or gas by assuming a definite shape independent of the containing vessel. When we come to examine more closely the structure of solids we observe notable differences. Certain substances, for example, in passing from the liquid to the solid condition, assume characteristic shapes, as alum, nitre, sugar, etc., while others harden without assuming distinctive shapes, as glass, wax, etc. [illegible] The former are [illegible] amorphous. Again, crys- [illegible] structure [illegible] cleavage, as [illegible] crystallization, as in gran- [illegible] The several systems [illegible] classified will be referred [illegible]

[illegible]

[illegible]

sion exists between the mercury and the glass. The water is drawn upward around the rod because its adhesion to the glass distinctly exceeds the cohesion of the liquid; the mercury adheres to glass much less strongly than it coheres, and hence it curves away from the rod. These attractions and repulsions have an interesting illustration in the phenomena known as *capillary*, observed when tubes of relatively fine diameter are dipped into liquids. If a glass tube be dipped into a liquid which wets it (or adheres), as in the case of water, the liquid will rise in the tube to a higher level than the surrounding surface, and the height is the greater the smaller the diameter. If, on the other hand, the tube be dipped into a liquid which does not wet it (or adhere), as in the case of mercury, the liquid will be depressed in the tube below the surrounding surface, and the smaller the diameter of the tube the greater the depression. These phenomena of rods and tubes are illustrated in Fig. 4. Many natural phenomena, such as the rise of moisture in rootlets and stems of plants, the rise of oil in a lamp-wick, the absorption of water by filter paper or sponges, are to be considered as illustrations of the principle of capillarity.

FIG. 4.



Capillary attraction and repulsion.

Diffusion of Liquids.—Closely connected with capillary phenomena are those of diffusion. If two liquids of different densities, but capable of admixture, be placed one above the other in the same vessel, they will begin to mix or diffuse through each other, even if the upper liquid be of less density than the lower. This will also take place though they be separated by porous partitions of various materials. But it is found that the rate of diffusion differs greatly for different substances. Many solids when in solution will diffuse rapidly, while others will diffuse with great slowness. The former class will be found to include most crystallizable solids, like salt, sugar, magnesium su etc., while the latter class includes uncrystallizable or amo substances, like starch, gums, gelatin, or glue. To the class the term *crystalloids* has been given, and to the lat term *colloids* (from the Greek word for glue).

Graham founded upon this property of unequal diffu the process of *dialysis*. A sheet of bladder or parchment is stretched tightly over the lower end of an open cylin inverted glass funnel. The mixture of liquids to be sep by dialysis is poured in above, and the dialyser supporte the lower end immersed in pure water contained in a larger vessel. The crystalloid substances will diffuse through the brane, and be found in solution in the outer vessel, whi colloids will remain in the inner vessel, or dialyser. The c has thus separated the crystalline arsenous acid from the c food material with which it may have been mixed in the sto and obtained it in a pure state for verification in cases o pected poisoning.

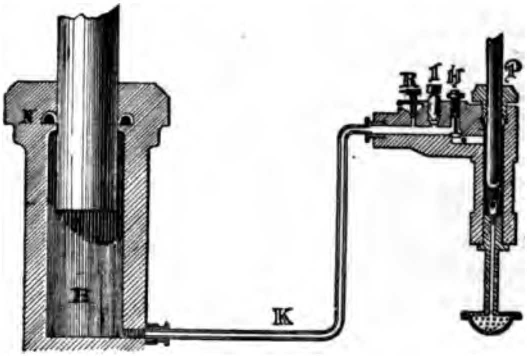
2. Pressure of Liquids.

Liquids are but slightly compressible, and with the re of the force causing pressure recover immediately their ori volume. For this reason and because of the ease with w their molecules are free to move, they readily transmit pre throughout their entire mass. This pressure is transm throughout the liquid equally in all directions, whether it is in which the force is applied or at an angle to it.

This is illustrated in the case of the sprinkling nozzle of a den hose, or similar apparatus, where the water is seen to i with equal force from all the apertures. Of course, if the pres in the one case is exerted over a larger area of surface tha the other, a different total force is felt in consequence. H we must multiply the intensity of the pressure per unit of face by the area of surface to get the total force exerted. He a pressure of five pounds per square inch exerted over a sur of sixteen square inches would be felt as a pressure of eig pounds upon that surface.

An important application of this principle of transmission pressure, and exertion of the same over a larger surface than t where it was applied, is found in the hydraulic press. This, shown in Fig. 5, consists of a small force-pump, in which wo a solid piston, P. When this piston is depressed by means o lever the valve *o* in the bottom of the cylinder is closed and the water is forced over through the connecting tube, K, into the larger cylinder, B. Here the pressure of the water upon the piston is exerted over an area perhaps a hundred times greater than that of the piston of the small pump, and hence the pressure is multiplied a hundred-fold. It must be remembered, however, that in our definition of energy and statement of the law of the conservation of energy (see p. 21) we said that energy could not be created any more than it could be destroyed. So in the hydraulic press, the energy developed in the larger cylinder is only seemingly greater than that exerted in the smaller cylinder. Though the pressure on the larger piston is one hundred times that applied to the smaller piston the former moves through $\frac{1}{100}$ of a foot while the latter moves through one foot. The hydraulic press is of great value in compressing cotton, hay, and other loose but bulky material, and in lifting heavy weights or moving machinery.

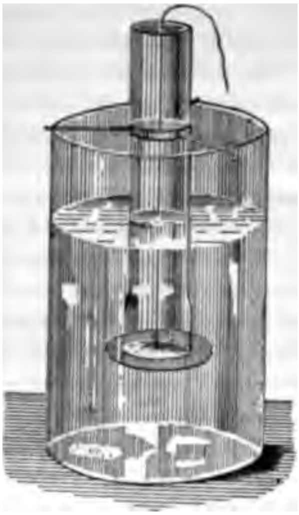
FIG. 5.



Hydraulic press.

In considering the pressure exerted throughout the body of a liquid we have so far disregarded the weight of the liquid itself. It is obvious that the weight of the upper layers of the liquid bears upon the layers immediately under them, and that the bottom layer therefore supports considerable weight. But because of the perfect mobility of the liquid molecules and the equal transmission of pressure in all directions, this pressure will be felt equally in all parts of the same horizontal layer, on the sides of the containing vessel, as well as upward and downward from that level. When the depth from the surface of th is twice as great, the intensity of the pressure will be twice a and so for different depths.

FIG. 6.



Upward pressure.

This pressure is entirel pendent of the shape of th containing the liquid. The d may be large or small withou ing the pressure, and in tl arises the seeming contra often called the *hydrostatic pa* A small body of water may e great a pressure upon the of the containing vessel as a larger body of water, if the of the liquid is the same in t cases. This is true, althou two bodies of liquid may wei erently because of the differe amount.

That the pressure in any h tal layer of a liquid is exerted e upward as well as downward o ally is an important fact, and is capable of a simple demonst If, as in Fig. 6, we take a glass cylinder, open at both en Argand lamp chimney with one end ground perfectly flat wi and, closing one end with an accurately fitting glass or metal lower it into a vessel filled with water, we find that the pl held in position by the upward pressure. Water may th poured into the glass cylinder until the level inside nearly or equals the level outside, when, the upward pressure having compensated for, the plate will drop off, because of its weig

Equilibrium of Liquids.—As every molecule in the body liquid is free to move, it is obvious that the force of gravit act upon all parts of the liquid equally, and the liquid will to rest only when each part of the liquid is in a position of s equilibrium. This is attained when the surface of the l assumes a position at right angles to the perpendicular or lir which the force of gravity is felt. We call the position s sumed a horizontal line, and the surface of a liquid free to res to this force therefore will always be horizontal, no matter the shape of the containing vessel. The level in several com nicating vessels will also speedily become the same, as equ of pressure soon establishes itself throughout the entire body of liquid, and the several surfaces come to rest in the same horizontal plane.

Just as the plumb-line is a practical device for quickly and easily determining the perpendicular line, so we have in the spirit-level a ready means of determining whether a surface is perfectly horizontal. It consists of a glass tube nearly filled with alcohol, a bubble of air only remaining. When this tube is mounted in a wooden or metal case, and the latter placed upon a horizontal surface, the air-bubble shows exactly in the middle of the upper surface of the tube, upon which a scale is marked. If the surface upon which the level is placed is not perfectly horizontal, the bubble moves towards one end or the other of the scale instead of remaining in the middle.

The Artesian well is an illustration of the principle of the equilibrium of liquids. In this case the strata which hold the water are shut in above and below by impervious layers of clay. At the same time, the water here accumulated has worked its way down from a much higher level. When the upper clay layer is perforated in sinking the well, the water rises, tending to reach the level from which it started.

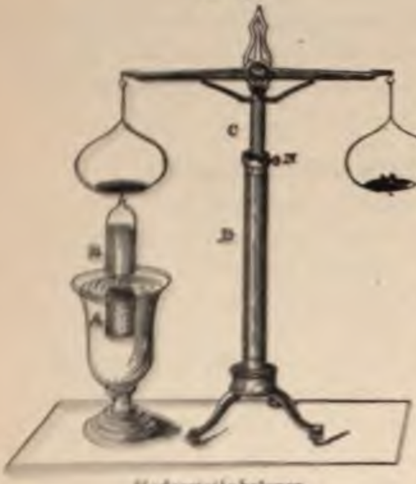
3. Pressure upon Bodies Immersed in Liquids.

We have seen that the pressure felt upon any molecule within the body of a liquid varies with the depth and is exerted equally upward as well as downward. We are now prepared to consider the effect of this pressure upon a solid body immersed in the liquid. As the horizontal pressures act from all sides, they may be considered as neutralizing each other. We have, therefore, only the pressures in a vertical direction to consider. It is obvious that upon the top of the solid there is exerted a vertical downward pressure, measured by the depth of this horizontal layer from the surface of the liquid, while against the under surface of the solid there is a vertical upward pressure, measured by the depth of that horizontal layer from the surface of the liquid. Of course, the pressure in the lower horizontal layer will be greater. Hence the solid will be pushed upward by a pressure greater than that which bears upon its upper surface, and greater by the weight of a column of the liquid equal in height to the difference in depth between the top and the bottom of the solid.

This result for the case of a body immersed in water is, therefo[illegible]essed by saying that the excess of upward pressure *is* *equal to the weight of the volume of water displaced by the immersed body.*

This excess of upward pressure (or *buoyancy*, as it is termed) obviously has its effect temporarily upon the weight of the solid body. The weight may be totally or partially overcome by this buoyancy, as the preceding considerations show us that *a body immersed in a liquid loses a part of its weight equal to the weight of the displaced liquid.* This statement may be very exactly demonstrated by the hydrostatic balance, as shown in Fig. 7. The solid brass cylinder A fits exactly in the brass cup B. The two are hooked together, suspended from the one pan of a balance, and counter-balanced exactly by weights placed in the other pan. A glass globe, or other vessel, is now placed in position around the brass cylinder, and water poured in gradually. The buoyant effect of the water causes the cylinder A to rise, so that the two pans of the balance no longer show equilibrium. If, however, water is poured into the brass cup B, the cylinder sinks, and when the cup has been filled, it will be found that the cylinder is just immersed, and that the two sides of the balance are exactly in equilibrium. Obviously the brass cylinder lost a portion of its weight exactly equal to the weight of an equal volume of water. This so-called principle of Archimedes gives us a convenient means of determining the volume of any solid which is not soluble in water. By weighing the solid first in air and then when immersed in water, we arrive at the weight of the equal volume of water displaced, and, as the relations of weight and volume of water are known (1 cubic centimeter of water at 4° C. weighing 1 gramme), we get the volume of the body which displaced the water.

FIG. 7.



Hydrostatic balance.

Its most important application, however, is in determining the relative weight of different solids and liquids, or, as it is termed, their *specific gravity*. In ordinary practice this relative weight is always based upon the weight of water taken as unity, so that what is desired is a comparison between the weight of any body and the weight of an equal volume of water. But, as we saw on the preceding page, we readily get this weight by noting the loss of weight experienced when a solid body is immersed in water. We, therefore, have the following simple rules for specific gravity based upon this principle:

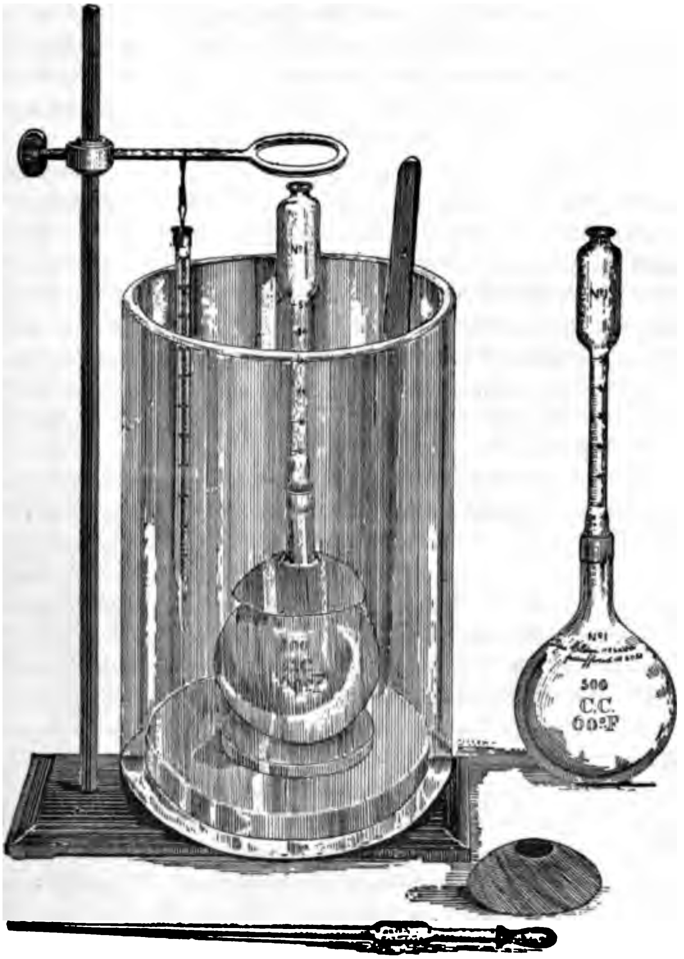
For Solids.—Weigh the body in air, then weigh again when immersed in water, and the weight in air divided by the loss of weight when weighed in water will give the specific gravity.

For Liquids.—Choose a solid insoluble both in water and in the liquid under examination; weigh this solid in air, and then when immersed in water and in the other liquid; divide the loss of weight when weighed in this other liquid by the loss of weight when weighed in water, and the result is the specific gravity.

In carrying out the specific gravity determinations of solids practically we have several methods to choose from. We may use the specific gravity balance, in which case the solid is suspended from one arm of the balance by a hair, or silken filament, and weighed first in air and then immersed in a small cup of water supported independently of the balance-pan and not touching it. Or, for powdered solids, the specific gravity flask may conveniently be used. This is a small glass-stoppered bottle, the weight of which, both empty and filled with distilled water, has been determined. For greater accuracy the ground-glass stopper is perforated, so that in fitting it to the bottle any excess of water may be forced out and wiped off with a piece of soft paper. In making a determination, the bottle is carefully dried, and, the powder having been placed in it, is weighed. This gives the weight of the solid in air. The bottle is then filled up with water, the excess being wiped from the top of the stopper, and weighed. The weight found is that of the powder, the bottle, and the original volume of water minus what has been displaced by the powder, which, of course, gives us the weight needed for the specific gravity calculation. In this determination by the aid of the specific gravity bottle, the water must be boiled previously, to expel the air, or the bottle, after filling in the powder and water, be put under an air-pump and exhausted.

A form of specific gravity bottle for very accurate work is that devised by Dr. Squibb and illustrated in Fig. 8. The bottle is weighted by means of a leaden collar, and the graduation on the stem allows of its being adjusted with great accuracy.

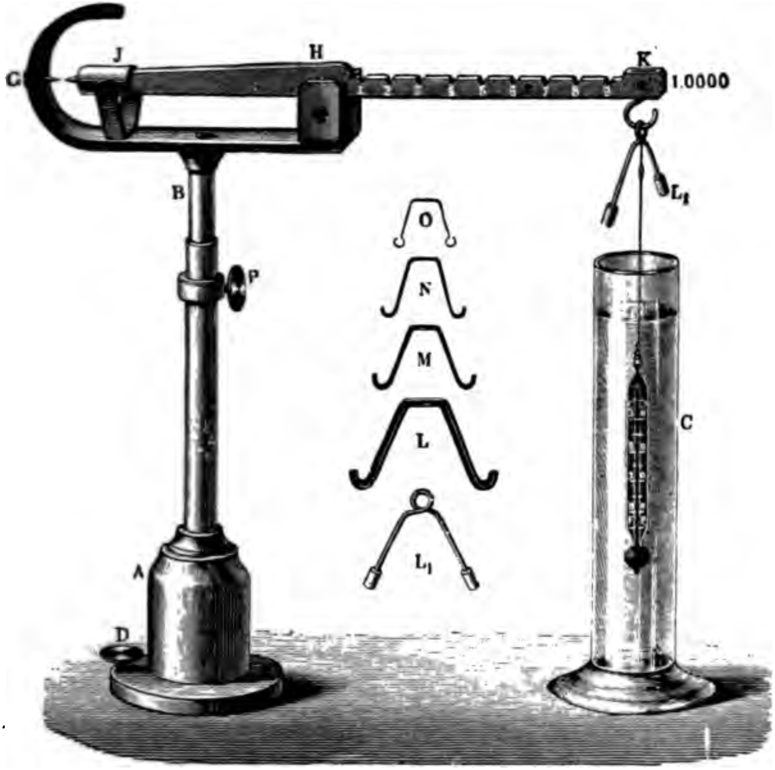
FIG. 8.



Apparatus for specific gravity, according to Dr. Squibb.

In the case of solids soluble in water, some other liquid, like naphtha or oil of turpentine, the specific gravity of which is already known, may be used. The specific gravity of liquids may be determined, as already indicated, by the balance. A special form of specific gravity balance that admits of rapid determination and great accuracy at the same time is the Westphal balance, illustrated in Figs. 9 and 10. The graduated arm of the balance has suspended from it a glass plummet carrying a thermometer, the weight of which is so adjusted that when sunk in distilled water at 15° C. and loaded with the rider L_1, the arm of the balance is exactly horizontal. The other adjustments of the weights necessary to establish equilibrium when the liquids used are heavier or lighter than water are shown in Fig. 10. In practice specific gravity is more conveniently determined by the aid of what are termed *hydrometers*. These are glass tubes loaded at the lower end with mercury or shot, so that they will float upright when immersed in a liquid. On the stem is marked a scale of degrees or equal parts. It is obvious that if one of these hydrometers sink to a certain depth in water, it will sink

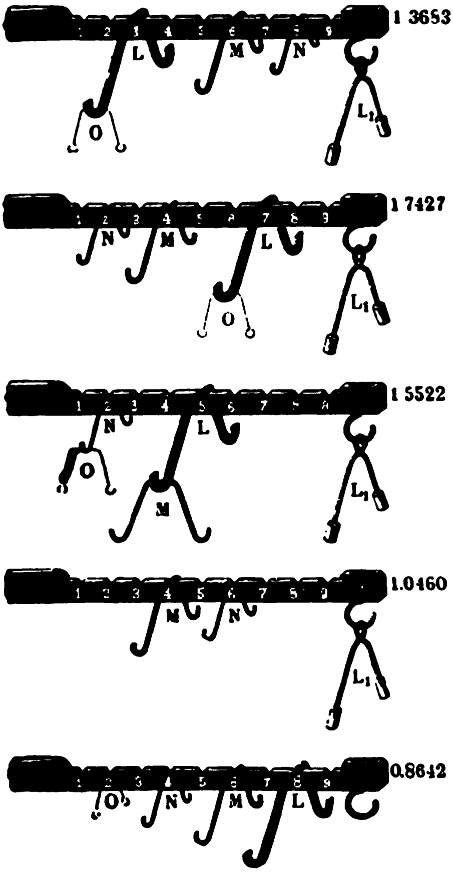
FIG. 9.



Westphal specific gravity balance.

still deeper in a liquid lighter than water, or float higher in one heavier than water. If then the point to which it sinks in water be marked 1 of the scale, the distance above this would be marked in decimal fractions less than 1, while the distance below would be marked in fractions greater than 1. In order to mark slight differences more accurately, a number of hydrometers are used in a set, of which several are weighted and graduated for liquids lighter than water and several for liquids heavier than water. Arbitrary scales are also in use for hydrometers, such as that of Beaumé for liquids heavier than water, that of Beaumé for liquids lighter than water, and those of Tralles, Twaddle, Gay Lussac, Beck, etc. Special forms for particular liquids are also used, as alcoholometers, salimeters, saccharometers, lactometers, etc.

FIG. 10.



Readings of the Westphal balance.

C. SPECIAL PROPERTIES OF GASES.

1. Attraction and Repulsion in Gases.

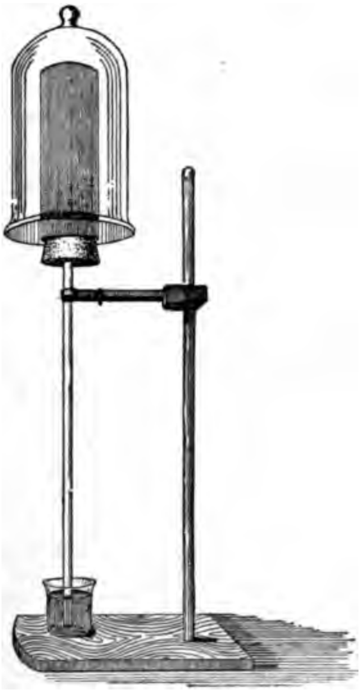
Expansion and Compressibility of Gases.—Gases have already been referred to as showing in the highest degree the tendency to expand because of the repulsion which exists between the molecules, causing them to separate more and more widely. Hence the volume of a gas is always dependent upon the temperature and pressure to which it is subjected at the time. This may be readily illustrated by placing a small rubber balloon partially distended with air or gas, but securely closed to prevent the escape of the gas, under the receiver of an air-pump (see p. 43). Upon exhausting the air from within the receiver, the balloon immediately distends and swells to several times its original bulk. This is, of course, due to the expansion of the gas under diminished pressure, as when the air is admitted again to the receiver of the pump the balloon contracts to its original dimensions.

The compressibility of gases under increased pressure is also capable of ready illustration by the aid of the pneumatic syringe. This consists of a tube of heavy glass closed at one end and provided with a tight-fitting solid piston. When this is pushed down the air may be compressed to a fraction of the original volume; but upon withdrawing this pressure the piston immediately rises and the air expands to its original volume.

An important fact to be noted is that there are limits to this contraction in volume under the influence of pressure. After a certain pressure has been reached (known as the *critical pressure*), the contraction of the gas causes a change of physical condition, and the gas becomes a liquid. Every gas has thus its critical pressure and temperature, the passing of which causes it to liquefy. This change of form will be referred to more fully under Heat.

Diffusion of Gases.—Gases possess the power of diffusing, whereby two gases of different densities rapidly become a homogeneous mixture, in the highest degree, as might be expected from the freedom of motion possessed by their molecules. Porous diaphragms of parchment, rubber, or unglazed pottery all allow of this diffusion.

FIG. 11.



Diffusion of gases.

It may be illustrated by the apparatus shown in Fig. 11. In this case, the porous cell shown fitted to the upright glass tube is filled with air, while a bell-jar containing hydrogen is held for a moment depressed around it. Gaseous diffusion immediately takes place through the walls of the porous cup, and the result is a mixture of hydrogen and air, both within and without the porous dividing wall. But hydrogen, as the lighter gas, diffuses more rapidly than the air, and the result is an excess of the gaseous mixture within the cup, and, in consequence, a bubbling out at the bottom of the upright glass tube.

The investigation of these phenomena of diffusion by Graham has shown that they take place according to a very simple law. He found that the rapidity of the diffusion of two gases of different densities was ***inversely as the square root of the densities of the gases.*** Thus, as hydrogen is about 14.5 times lighter than air, it will diffuse nearly four times faster than air.

Absorption of Gases by Liquids and Solids.—These two cases, while showing some points of resemblance, are generally based upon different physical operations. In the case of the absorption by liquids, we must suppose that, under the influence of a powerful attraction, the gas which is absorbed is first liquefied, and then taken up in a physical admixture. This attraction is dependent to a considerable degree upon temperature, but with that limitation it is fixed and uniform for the particular gas and the liquid which acts as its solvent. Thus, the nitrogen and oxygen of the atmosphere are soluble in water in different proportions from those in which they exist admixed in air.

Numerous examples of the solubility of gases in liquids will be found later in the discussion of the chemical elements and their compounds. In some cases the action is believed to be purely a physical one, as in the case of oxygen just mentioned; in other cases it is probably due, in large part, to the forming of a chemical combination, such as a hydrate, as in the case of the absorption of ammonia, chlorine, carbon dioxide, etc. The absorption of gases by solids, on the other hand, is considered to be due, in the main, to the attraction which causes the gases to deposit in a more or less thick layer of condensed gas upon the surface of the solid. Porous bodies which expose a large surface are, therefore, especially adapted for the illustration of this. Freshly prepared wood charcoal, for instance, at ordinary temperatures, will absorb ninety volumes of ammonia gas and smaller amounts of other gases. It is interesting to note that, in general, the absorption is greatest in the case of those gases which are most easily liquefied. Certain metals, although compact in structure, possess the power of taking up or *occluding* many times their volume of certain gases. This is shown in the case of platinum and palladium with hydrogen, and of iron and nickel with carbon monoxide. It is probable that in the former case true metallic alloys are formed by the union of hydrogen with the metals, and in the latter that a chemical compound is formed for the time being.

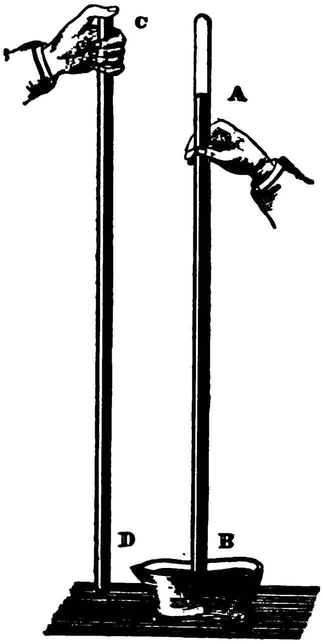
2. Pressure Exerted by Gases.

Weight of Gases.—That, despite their apparent lightness and expansibility, gases possess weight is easily capable of proof. If a glass globe, provided with a brass cap and stop-cock, be attached to one pan of a balance and accurately counterbalanced when filled with air, on removing it and exhausting the air with the aid of an air-pump, it is found that it has lost notably in weight. This loss represents the weight of the air pumped out of the globe. In the same way, all gases can be shown to have appreciable weight. Their relative weight is usually expressed by referring them to an equal body of air as unity, and is termed their specific gravity. Their relative weight referred to hydrogen as unity, we will see later, is usually termed their density.

The Atmosphere and its Pressure.—The pressure exerted by gases can be advantageously illustrated by a study of the atmosphere. This is the layer of air which surrounds the earth on all sides. That it has weight, and in consequence exerts pressure, can be shown by a variety of experiments. A piece of wet bladder is stretched tightly over the open end of a strong glass cylinder, the other end of which is fitted accurately to the plate of an air-pump. If, after the bladder has dried, the air be exhausted from within the cylinder, the atmospheric pressure exerted upon the outer surface of the bladder presses it in, and finally bursts it with a loud report as the air suddenly enters the cylinder. The Magdeburg hemispheres, two disks of brass accurately fitted together so that the whole forms a hollow sphere, and capable of being exhausted through the stem of one of the hemispheres, which is provided with a stop-cock, also illustrate atmospheric pressure. When the air in the interior has been pumped out and the stop-cock closed, it is found impossible to separate the two hemispheres except by the exertion of great force.

These experiments show that the atmosphere presses upon everything upon the earth's surface with a weight which must be quite considerable. How much this pressure measures was first shown in the experiment of Torricelli. This is illustrated in Fig. 12. A glass tube about a yard long and sealed at one end is taken and filled with mercury. Having closed the open end of the tube with the thumb, the tube is inverted and dipped into a small vessel filled with mercury. The column of mercury is seen to fall, and after some slight oscillation remains stationary at about thirty inches above the level of the mercury in the outer vessel. No matter how long the tube may be, or what its diameter, this height of mercury column is always observed. Only one explanation of this fact is possible. It is that the atmospheric pressure will support a column of mercury some thirty inches in height and no more. The space above the mercury in the inverted tube is a vacuum, and hence there is no counterbalancing pressure upon the mercury at this point. If the upper or closed end of the tube be provided with a stop-cock and air be admitted, the mercury in the tube will immediately fall and come to the same level as that in the outer vessel.

FIG. 12.



Torricellian vacuum.

When water is used instead of mercury it is found that the atmospheric pressure will support a column thirty-four feet in height, which is about 13.6 times as high as the mercury column. But mercury is 13.6 times heavier than water, so that the weight of the two columns is the same in the two cases, and is supported by the exertion of the same pressure. To reduce this to a simple numerical expression, let us assume that the area of the tube in the experiment with mercury is a square inch. We thus have thirty cubic inches of mercury supported by the pressure of the atmosphere. A cubic inch of mercury weighs 3433.5 grains, or 0.49 of a pound, so that the weight of the thirty inches is 14.7 pounds. It is customary to consider the atmospheric pressure as equalling in round numbers fifteen pounds upon a square inch of surface, and this is often referred to as a pressure of one atmosphere. The instruments used for measuring atmospheric pressure are called

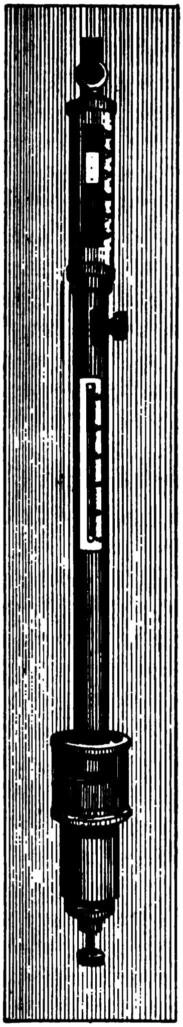
Barometers.—The simplest form of barometer, of course, is the straight tube of Torricelli as just described. This tube, suitably mounted in a frame on which a scale has been constructed and dipping into a small cup filled with mercury, constitutes the cistern barometer. A convenient form of cistern barometer is shown in Fig. 13. Another form, preferred for many purposes, is the siphon barometer, shown in Fig. 14. In this case the tube has two unequal branches, of which the longer is closed, and the shorter, acting as the cistern, has an opening communicating with the air. There are two scales, one at either end, so as to note the height of the mercury in either branch. The distance between the upper and lower levels constitutes the barometric column. At the sea-level this is almost exactly thirty inches of the English scale, or 760 millimeters of the metric scale. At any considerable height above the sea-level, of course, the pressure is less, because the lower layers of the atmosphere have been passed, and, as these layers are denser than those above them, the barometric reading will be notably less. Thus, at a height of 3.4 miles, or 17,952 feet (the height of some of the Alpine peaks), exactly one-half of the atmospheric pressure is felt, as indicated by the barometer reading of fifteen inches.

Still another form of barometer, and the one most generally used by travellers in determining the height of mountains, on account of its lightness and portable character, is the aneroid barometer. This is a flat, thin-walled, circular box of corrugated metal, exhausted of air and then hermetically sealed. The variations of the atmospheric pressure upon the sides of this box cause a system of levers to register by means of a needle running over a graduated dial face. The graduation must, of course, be made by comparison with a standard mercurial barometer.

3. Pressure on Bodies Immersed in Air.

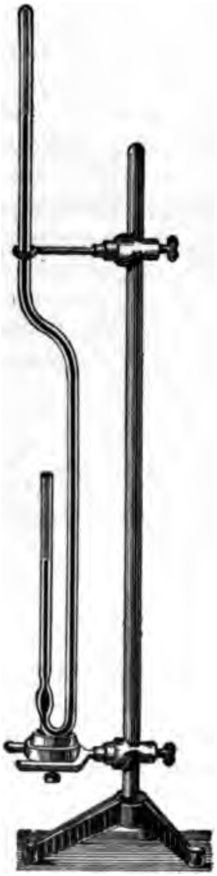
Buoyancy of Gases.—The principle of Archimedes (see p. 32), whereby a body immersed in a liquid loses a portion of its weight equal to the weight of the displaced liquid, is equally true of gases, and that they possess buoyancy or supporting power upon bodies immersed in them is easily shown. A small scale-beam is taken, capable of being put under the bell-jar of an air-pump, and from one arm of this a hollow copper sphere is suspended, counterbalanced by a small weight attached to the other arm. When this is put under the bell-jar and the air exhausted, the hollow sphere, deprived of the buoyant effect of the air, sinks

FIG. 13.



Cistern barometer.

FIG. 14.



Siphon barometer.

and appears to be heavier than the small weight, which felt the buoyant effect of the air much less because of its smaller bulk.

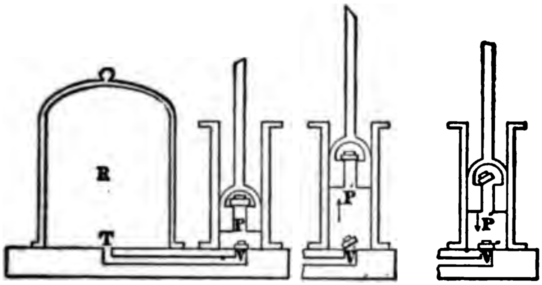
An important application of the buoyancy of the air is the use of balloons. These are simply hollow spheres of light but impermeable material, such as silk coated with caoutchouc or other varnish, which enclose a large volume of some light gas, like hydrogen or illuminating gas, and displace a corresponding volume of air. The weight of the balloon and its equipment, together with that of the volume of gas contained, subtracted from the weight of the volume of air displaced, will give us the ascensional force of the balloon.

Great heights have been attained by the use of balloons: Mr. Glaisher in 1861 ascended to a height of some 36,000 feet, as indicated by the barometric reading of about seven inches; but as yet it has not been found possible to direct their movements with any certainty.

4. Apparatus Based upon Atmospheric Pressure.

The Air-Pump.—The exhaustion from any given space of the air contained, or the removal of the atmospheric pressure, not only is important as allowing us to demonstrate the effects of this pressure, but is a necessary operation in many manufacturing processes, as in evaporation of liquids in vacuo, the exhaustion of globes for incandescent electric lamps, operating the condensers of steam-engines, etc. We will here refer only, however, to the portable forms of exhausting pumps for production of a vacuum.

FIG. 15.



Air-pump.

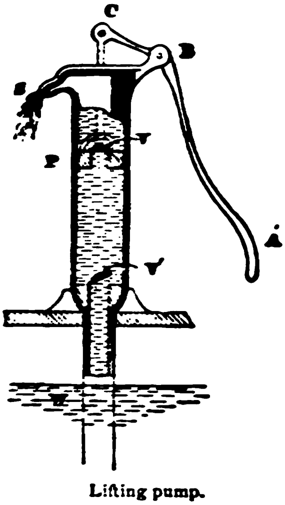
Fig. 15 gives a sectional view of the common form of air-pump. If we start with the piston P at the bottom of the cylinder, as it is drawn up the valve V′ opens upward and air is drawn out of the receiver R. When the piston begins to descend, the valve V″ closes and the valve in piston P″ opens, letting the air escape into the space above the piston. The air can thus be considerably rarefied by a few strokes, but it is impossible to produce a perfect vacuum, owing to the difficulty of securing perfectly fitting joints for the apparatus.

A more perfect vacuum is attained by the aid of the Sprengel mercury pump. This consists simply of a vertical tube of narrow bore, something over a yard in height, a few inches from the top of which a lateral tube is made to connect perfectly air-tight. If now mercury be poured into the vertical tube by the aid of a funnel, in falling it draws the air from the vessel connected with the lateral tube until a complete vacuum has been established therein, when a column of mercury thirty inches in height will stand in the vertical tube. These pumps are used exclusively in producing the vacuum needed for incandescent electric-light globes.

Condensing Pumps.—By a different arrangement of the valves in the cylinder and side-tube, instead of exhausting a given space, additional air may be forced in and so brought under considerable pressure. A condensing pump is also useful in condensing other gases than air, as in forcing carbon dioxide under pressure into solutions.

Lifting and Suction Pumps.—An important application of the principle of atmospheric pressure is seen in the pumps devised for the lifting of water from wells and cisterns. One of the common forms is illustrated in Fig. 16. The action here exactly corresponds to that in the cylinder of the air-pump. As the piston P is drawn up, the valve V′, known as a clack-valve, opens upward, and air with water following it is drawn up into the cylinder. As the piston descends, the valve V′ closes and V opens. After a few strokes the water is lifted by this action from the depth W to the cylinder and there remains, filling the whole length of the tube. It is obvious that the action of the piston first exhausts the cylinder of air, and that the water rises into the vacuum thus

FIG. 16.



Lifting pump.

formed, where it remains unless the leakage of air into the cylinder causes the water to fall again to the level of that below. Other forms of pumps combine the principle of exhaustion and pressure, and thus can deliver a continuous stream of water.

The Siphon.—This is simply a tube bent at an acute angle, open at both ends, and with legs of unequal length. If the siphon be filled with liquid and the longer end closed temporarily, on dipping the shorter leg into the liquid contained in an open vessel a flow begins when the longer leg of tube is unstopped, and the liquid will drain from the vessel until the level falls below the end of the short leg. The explanation of the action of the siphon is simple. When it is in action, the pressure on the surface of the liquid in the vessel is the atmospheric pressure minus the vertical distance from this surface to the top of the shorter leg of the siphon, while the pressure on the liquid where it is flowing out is the atmospheric pressure minus the vertical distance from the point of escape to the bend at the top of the longer leg. This latter pressure is less than the former, hence the liquid continues to flow out as long as this inequality continues.

CHAPTER III.

RADIANT ENERGY.—I. Heat.

I. THE NATURE OF HEAT.

HEAT is a form of energy due to molecular vibration. This vibration seems to be taking place in greater or less degree in all bodies, and, when communicated to the ether which fills all space around the vibrating body, is transmitted to the nerves of sensation, and so is felt as heat. The presence of air is not essential for this transmission of heat vibrations, as they are transmitted equally in vacuo as in air. When these vibrations become more rapid the heated body may become luminous, and this manifestation of radiant energy is called light. Electrical energy seems to be due to vibrations of the same nature, but of still greater rapidity of movement. Such is the undulatory or vibratory theory of heat and light. The fact that one of these related forms of energy can be changed readily into the others, and that all of them can be produced from mechanical energy, renders this theory a very probable explanation of the observed phenomena.

An older theory that heat as well as light was due to the emission of material particles from heated bodies, or sources of heat, is now practically abandoned. Similar statements with regard to the existence of a supposed material substance called caloric are now considered as devoid of any foundation of truth.

II. SOURCES OF HEAT.

1. Physical Sources.—By far the most important source of heat known is the sun's radiation. What the source of the sun's heat may be is not known, nor can any exact estimates be made as to the temperature existing upon the sun's surface. The quantity of heat received upon the whole surface of the earth in any given unit of time, as in a day, is, however, enormous. Not only is it the greatest of the present sources of heat, but by its past activity it has been the means of accumulating for us the immense stores of coal, petroleum, and other valuable heat-producing substances used at present as fuel.

The earth possesses also a heat of its own, readily noted as we descend to any considerable depth below its surface, and made evident to us in hot springs and volcanoes. The explanation most generally accepted for this is that the earth has cooled from a much more highly heated state, probably that of an incandescent gas, and that, while a hard crust has formed upon the surface, the interior of the globe is yet in a molten and liquid state.

2. **Chemical Sources.**—Most forms of chemical combination, as we will see later, are accompanied by the development of heat in definite amounts, or are *exothermic*. Hence every case of combustion going on about us in nature contributes to the development of heat. This includes the rapid combustion of all forms of fuel, and the slow combustion or decay of organic matter. It includes also the respiration of all kinds of animals, and the processes of assimilation of food equally due to chemical and heat-producing changes. Those forms of fuel which are richest in the elements carbon and hydrogen possess the greatest value as fuel, as by the oxidation of these elements the maximum of heat can be developed. Hence the value for heating purposes of the several varieties of coal, of petroleum, of hydrocarbon gases, and of so-called "water-gas."

3. **Mechanical Sources.**—Friction and percussion are among the commonest of the methods by which heat is developed. The old device of obtaining sparks from a piece of flint and a steel, and the still older one of the savage of rubbing together two dry sticks to kindle a fire, are illustrations of the development of heat by friction. The "hot-box" on a railway car, where the heat developed by the friction of the car-axle in its box often suffices to ignite the oil-soaked waste, is also an illustration. The striking of the blacksmith's hammer upon the anvil readily illustrates the heat developed by percussion. In this case the energy of the mass of the hammer in descending is changed when it strikes into the molecular energy of the particles known and recognizable by the senses as heat.

Mechanical Equivalent of Heat.—The fact that visible mechanical or mass motion may be changed into molecular motion, or heat, suggests that a mechanical equivalent may be established for a given development of heat. This idea, first brought forward by Mayer, was experimentally established by Joule. He determined the number of foot-pounds (see p. 20) of energy equivalent to a unit quantity of heat. He used a copper vessel filled with water and provided with brass paddle-wheels, which were set in motion by the falling of weights. The weights being known and the space through which they fell, as well as the difference in temperature of the water at the beginning and at the end of the fall, the amount of fall corresponding to an increase of one degree was readily calculated. The result expressed in English units is that to raise one pound of water one degree Fahrenheit requires 772 foot-pounds, or to develop one degree Centigrade requires 1390 foot-pounds.

III. Effects of Heat.

If we refer for a moment to the explanation given as to the nature of heat, we can conjecture what the effects of the application of heat to a body would necessarily be. In the first place, the vibrations already existing between the molecules or particles of the body will be increased in rapidity, and the body, to use the common expression, becomes hotter. This is made evident by rise of temperature, appreciable by the senses or by more accurate recording instruments. In the second place, these vibrations will increase not only in rapidity but in amplitude, and the body expands, the force of cohesion having been weakened while that of repulsion tends more strongly to drive the molecules apart. In the third place, this loss of cohesive power may go so far that change of physical condition results. A solid body under the influence of heat may fuse or liquefy, and a liquid when heated may boil and be entirely volatilized. We shall take up these several effects of heat in succession for more detailed study.

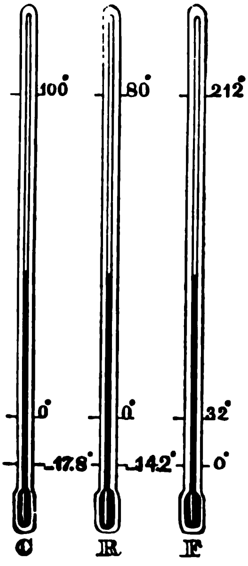
1. Rise of Temperature.—This is the first and most general effect of heat. Indeed, it might be called the invariable effect except for the case which will be referred to later, when the heat applied is consumed in doing the work of changing the physical condition of the body, or, as it has been termed, is rendered *latent*. In this case it does not show in the raising of the temperature of the body.

Rise of temperature is in some cases appreciable by the senses, but more delicate means of distinguishing are clearly obtainable in the use of what are termed *thermometers*, or heat-measurers. These usually depend upon the expansion and contraction under the influence of heat and cold of a liquid or gas, but the expansion and contraction of metals are also availed of at times.

The ordinary thermometer is that in which mercury is used. It consists of a glass bulb of spherical or cylindrical shape connected with a fine capillary tube or stem. The bulb and part of the stem having been filled with mercury, this is boiled to expel the air and the tube is sealed up. To establish a scale for the thermometer when thus filled, two fixed points are needed. One is obtained by immersing the bulb in melting ice, and the other by suspending it in steam from water boiling at normal pressure, and these points are permanently marked upon the glass. Between these two, a scale is now to be made and the individual divisions or degrees of the scale are to be marked.

Three scales have been proposed and are now in more or less common use. The Fahrenheit (used commonly in England and in the United States), the Réaumur (formerly used in Germany and used still in Sweden and Denmark), and the Centigrade or Celsius (used commonly in Europe, as well as in scientific literature generally). The two fixed points before referred to serve equally for all of these, but the method of dividing the space between the two points is different in each of them. The distinction between the several scales is shown in Fig. 17. In the Centigrade and the Réaumur scales the lower fixed point (the melting point of ice) is called zero, while in the Fahrenheit scale it is put at the 32d division of a scale which starts lower. The upper fixed point (the boiling point of water) is taken as 100 degrees of the Centigrade scale, as 80 degrees of the Réaumur scale, and as 212 degrees of the Fahrenheit scale. Consequently, the space between the two fixed points is divided into 100 degrees in the Centigrade scale, into 80 degrees in the Réaumur scale, and into 180 degrees in the Fahrenheit scale. Divisions of the same value are continued both above and below the fixed points upon each of the several scales, degrees below zero being indicated by the sign minus. One degree of the Centigrade scale (expressed 1° C.) will equal $\frac{4}{5}$ of a degree Réaumur (1° R.) and $\frac{9}{5}$ of a degree Fahrenheit (1° F.).

FIG. 17.



Comparison of thermometer scales.

The conversion of readings of the Centigrade scale into the corresponding readings of the Réaumur scale, and *vice versa*, is easily effected by the aid of this fraction, using the expressions $C.^\circ \times \frac{4}{5} = R.^\circ$, and $R.^\circ \times \frac{5}{4} = C.^\circ$.

In the case of the Fahrenheit scale, the problem is not quite so simple, as the zero of this scale does not agree with that of the other two, and instead of the lower fixed point of the scale being placed at zero it is 32 degrees above zero. This inequality is easily overcome, however, and to convert Fahrenheit readings into Centigrade we use the expression $(F. - 32)\,\frac{5}{9} = C.$, and to convert Centigrade readings into Fahrenheit, $\frac{9}{5}\,C. + 32 = F.$ When the minus sign is prefixed to a reading, this must be taken into account in adding or subtracting the 32.

The Centigrade scale is readily seen to be the most convenient as well as the most philosophical of these several scales, and it has practically displaced the other two in all exact and scientific work.

The limits of use of the mercurial thermometer are, of course, reached as we approach the freezing or the boiling point of mercury. The lower limit of accuracy is —36° C., as mercury freezes at —40° C.; the upper limit is about 300° C., as mercury boils at 350° C.

For low temperatures, therefore, the alcohol thermometer is used, as this liquid does not solidify at extreme low temperatures.

For high temperatures the air thermometer is used, and when necessary the bulb is made of platinum. The stem in this case is not sealed, and a small index of colored sulphuric acid moves along as the air expands or contracts. For extremely high temperatures pyrometers are also used, in which the variation in electrical conductivity of a strip of platinum is made to indicate the difference in temperature.

2. Expansion in Volume.—This is due to the fact that the more rapid vibration of the particles of a body under the influence of heat weakens the force of cohesion, and hence tends to separate the molecules more widely. It shows itself in solids, liquids, and gases, although, as might be expected, most largely in the last named.

With solids we have to consider the case of both linear and cubical expansion. The coefficient of linear expansion is the elongation per unit of length for a rise of temperature of one degree Centigrade, while the coefficient of cubical expansion is the increase per unit of volume for a similar rise of temperature. These coefficients vary with different solids, as for glass and the different metals, but a fixed relation exists between the coefficients of linear and cubical expansion for one and the same solid, viz., the coefficient of cubical expansion is three times that of linear expansion. The coefficients of the expansion of metals vary with their physical condition, being different for the same metal according as it has been cast or hammered and rolled, hardened or annealed.

We meet with numerous practical illustrations and applications of the expansion of solids. Furnace bars must not be fastened tightly into masonry at both ends, lest they split the masonry by expanding; water-pipes are provided with telescopic joints to allow of expansion; in laying rails for railways, space must be left between two connecting rails for expansion; iron tires are put upon wagon-wheels while highly heated, so that in contracting they may tighten all parts of the wheel; hot liquids cannot be poured into vessels of thick glass without danger of breaking, because of the unequal expansion of the glass.

Liquids expand in general more than solids under the influence of heat. In measuring the expansion of liquids a distinction must be made between the apparent expansion of a liquid contained in a vessel of glass, which itself expands by heat, and the real expansion of the liquid irrespective of the expansion of the containing vessel. The force exerted by liquids in expanding is very great, as might be expected from the difficulty experienced in attempting to compress them.

Water presents an important exception to the rule that liquids expand uniformly with the increase of heat and contract with cold. When water is cooled down gradually from the ordinary temperature, it contracts until 4° C. (39° F.) is reached, when it begins to expand, and continues to increase in volume until it freezes at 0° (32° F.). Hence it shows its maximum density at 4° C. This is of the greatest importance in nature. As the water in lakes and rivers cools in winter, it contracts and sinks until the temperature of 4° is reached. After this the cooler layer becomes lighter and remains on the surface, where it congeals and forms ice, which in time protects the water below from the extreme low temperature to which the air may be reduced. In this way fish and other fresh-water animals are able to live through severe winters without experiencing any lower temperature than 4° C. The expansion of water in cooling to form ice also plays a very important part in the operations of nature. More than any other force it reduces rocks to fragments by freezing in crevices and splitting off small particles. It bursts iron and leaden pipes and other vessels in which it may be when these are exposed to low temperatures.

The expansion of gases under the influence of heat takes place very regularly, so that the volume of a gas is dependent upon its temperature as well as upon the pressure to which it may be subjected. Hence gaseous volumes for comparison are always reduced from the observed temperature and pressure to a uniform standard in these two respects. This standard is 0° C. and 760 millimeters of pressure, to which gaseous volumes are reduced in all cases of accurate measurements. That air when heated expands and becomes specifically lighter is recognized in all systems of ventilation and in creating a draft for purposes of combustion.

Unit of Heat and Specific Heat.—The quantity of heat necessary to raise one pound of water through one degree Centigrade is called a *thermal unit.* It is obvious that twice the quantity of heat will raise one pound of water through two degrees or two pounds of water through one degree. Similarly, if we mix one pound of water at 100° C. with one pound of water at 0° C., we will have two pounds of water at 50° C., as the one pound at zero will take from the other pound at 100° fifty heat units, and the two pounds will thus be brought to a common temperature. On the other hand, if a pound of mercury at 100° C. is mixed with a pound of water at 0° C., the temperature of the mixture will only be about 3° C. While the mercury has cooled through 97 degrees the water has been raised only 3 degrees. We see from this that a given weight of water requires about 32 times as much heat as the same weight of mercury to produce the same elevation of temperature. Other substances are found to vary similarly, and hence each substance must be considered to possess a definite heat capacity, or *specific heat.* This is ascertained by dividing the amount of heat required to warm a given weight of any substance one degree by the amount required to heat an equal weight of water one degree.

3. Change of Condition.—We have already stated that if the application of heat to a body be continued, rise of temperature and expansion in volume are often followed by change of condition. Let us first note these results in the case of solids. All of the metals and many other solids have definite temperatures at which, under the influence of heat, they fuse or liquefy, the force of molecular cohesion having been overcome by the increased rapidity of the vibrations of the molecules. Some substances are very refractory, or incapable of fusion, except at excessively high temperatures, and some, chiefly those of complex chemical composition, such as paper, wood, and vegetable and animal fibres and tissues, are decomposed without fusion. With these exceptions we may consider fusion a regular change which solids will undergo when the appropriate temperature is reached. Two definite general laws can, indeed, be stated for all fusions.

1. Every substance begins to fuse at a certain temperature, which is invariable for each substance if the pressure be constant.

2. Whatever the intensity of the source of heat, from the moment fusion commences the temperature of the body ceases to rise and remains constant until the fusion is complete.

The range of temperature shown in the fusing points of solids is very great, varying from —38.8° C. for mercury to 1900° C. for platinum.

When metals are fused together they generally form a homogeneous mixture which often possesses properties quite different from those possessed by either of the metals singly. Such mixtures are called *alloys*. They are generally more fusible than either of the metals of which they are composed. For instance, Rose's fusible metal, consisting of 4 parts of bismuth, 1 part of lead, and 1 part of tin, melts at 94° C., while its most fusible constituent, tin, melts at 228° C. Wood's fusible metal, consisting of 1 or 2 parts of cadmium, 2 parts of tin, 4 parts of lead, and 7 or 8 parts of bismuth, melts between 66° and 71° C. These alloys are largely used for solders and in taking casts.

The second law of fusion stated above obviously requires some explanation. If a pound of water at 80° be mixed with a pound of water at 0°, the result will be two pounds of water at 40°. But if a pound of water at 80° is mixed with a pound of ice at 0°, the two pounds of water obtained will have a temperature of 0°. The pound of ice in melting has used up the 80 degrees of heat originally possessed by the pound of water, so that this latter pound and the pound resulting from the melting of the ice are equally at 0°. These 80 degrees of heat have disappeared as sensible heat. But, as before stated, energy cannot be destroyed. It must, therefore, still be present, although stored up as potential energy under the name of *the latent heat of fusion*. That these 80 degrees of heat have been temporarily absorbed without raising the temperature of the water produced from the ice is capable of proof, as when the pound of water again becomes ice this absorbed heat is all given out, and can by measurement be shown to be the equal of that which disappeared before. Every liquid has its own latent heat. That of water, as established by the above experiment, is 80° C.

Solution of Solids in Liquids.—Many liquids act as solvents, —that is, solid bodies are said to dissolve in them, and for the time being pass into the liquid state. This often takes place at ordinary temperatures, so that the solid liquefies without the application of heat. What under ordinary circumstances would require the application of a considerable amount of heat here takes place under the impelling influence of some other force. What this is we do not know very exactly The phenomena of solution and of fusion are so analogous that physicists agree that solution of solids in a liquid is a case of fusion and mechanical admixture. During solution, as during fusion, a certain quantity of heat is rendered latent, or stored up, so that the solution of a solid always lowers the temperature of the liquid acting as solvent. Many solids of complex composition, like gums, sugar, and other organic substances, which, as before stated, cannot be fused by mere application of heat without decomposition, are easily soluble in water. Others insoluble in water are soluble in alcohol and ether. Evidently these solvents have a powerful effect upon the solids mentioned, forcing them into the liquid state and then making a homogeneous physical admixture.

Solidification of Liquids.—Just as change of condition takes place when solid bodies fuse under the influence of heat or dissolve in liquids, so the reverse change may take place, whereby the liquid may resume the solid form, either from fusion or from solution. For this change the following laws, analogous to those before stated for fusion, may be given :

1. Every body under the same pressure solidifies at a fixed temperature, which is the same as that of fusion.

2. From the commencement to the end of the solidification the temperature of a liquid remains constant.

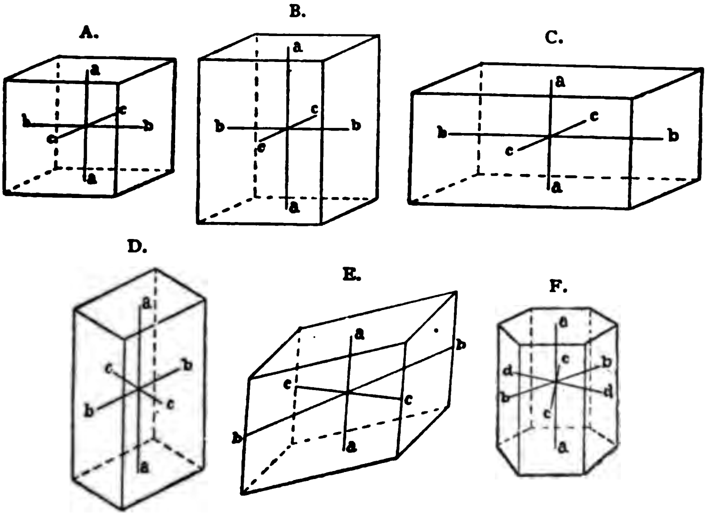
This second law, it will be seen, is the counterpart of the law of fusion already explained involving the absorption or storing up of heat. Just as in the other case, no matter what the heat applied, the temperature of the melting solid remained constant until the operation was completed, so in this reverse change, no matter how intense the cold, the giving out of the potential heat energy stored up in the liquid prevents any lowering of the temperature until the solidification is complete.

This principle of the storing up of heat in the liquefaction of a solid and giving it out in the reverse change of solidification of the liquid has a great importance in the economy of nature. The first severe cold of winter does not cause the streams and lakes to freeze up suddenly and completely, because for every pound of ice produced eighty heat units are given out and have a notable retarding influence upon the freezing operation ; similarly the first warm days of spring do not instantly melt the accumulated snow and ice of the mountain valleys, because for every pound of ice melted eighty heat units must be taken up and withdrawn from present effect upon the temperature.

It is obvious that, as the phenomena of solution are analogous to those of fusion, so we may have as the counterpart of solidification from fusion a solidification from solution. In the former case change of temperature is the occasion of the solidification ; in the latter, besides this cause, we may have the removal by evaporation or otherwise of the solvent as the determining cause of the solidification.

Crystallization.—In both cases, and notably in solidification from solution, because slower, the substance in assuming the solid state may take a characteristic geometric form, known as a crystal.

Fig. 18.



Systems of crystallization.

While these crystallized solids appear to vary greatly in appearance, they may all be arranged in six groups of geometric forms, which are therefore termed the six crystallographic systems. These are the *regular* or *isometric*, the *tetragonal*, the *orthorhombic*, the *monoclinic*, the *triclinic*, and the *hexagonal* systems, each of which is distinguished from the others by the difference in the axes or lines of growth around which the crystal develops. These are shown in their simplest forms in Fig. 18. To the first or isometric system, A, belong such forms as the cube and octahedron or regular pyramid, and in this system crystallize the diamond, magnetic oxide of iron, alum, etc.; to the second system, B, belong the square pyramid and prism, and in it crystallizes sulphate of nickel, etc.; to the third system, C, belong the rhombic pyramid and prism, and in it crystallize barytes, sulphur, yellow prussiate of potassium, etc.; to the fourth system, D, belong the oblique pyramid and prism, and in it crystallize gypsum, cane-sugar, etc.; to the fifth system, E, belongs the doubly oblique pyramid, and in it crystallize copper sulphate, potassium dichromate, etc.; to the sixth system, F, belong the hexagonal pyramid and prism and the rhombohedron, and in it crystallize bismuth, quartz, calcite, etc. Bodies which solidify from fusion or solution without any appearance of crystallization are said to be *amorphous*.

Freezing Mixtures.—The absorption of sensible heat when solid bodies pass into the liquid state is often availed of to produce artificial cold. Thus, if the liquefaction of a solid can be accelerated by the action of the other ingredients of the mixture, it will absorb notable quantities of heat from surrounding bodies, and so act as a refrigerating or freezing mixture. Thus, a mixture of two parts of powdered ice or snow and one part of salt will rapidly reduce the temperature of substances around which it may be packed. The salt at once forces the liquefaction of the ice, thereby lowering the temperature, and the water from this liquefaction of the ice dissolves salt, again lowering the temperature, so that their combined action is quite energetic in the way of absorbing heat from surrounding bodies.

Mixtures of certain salts and acids also act as freezing mixtures, as when 8 parts of solid sodium sulphate and 5 parts of hydrochloric acid are taken, 3 parts of sodium sulphate and 2 parts of dilute nitric acid, or 9 parts of sodium phosphate and 4 parts of dilute nitric acid. All of these reduce temperature because of the rapidity with which the salt is liquefied by admixture with the acid.

Evaporation and Ebullition.—Evaporation is the slow production of vapor at the surface of a liquid. It may take place at temperatures much below the boiling-point of the liquid. Ebullition is the rapid production of vapor, and indicates that the point has been reached at which the liquid is changing into a vapor.

The laws of ebullition have been determined as follows:

1. The temperature of ebullition, or the boiling-point, increases with the pressure.

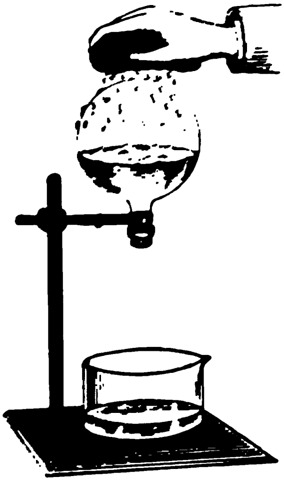
2. For a given pressure, ebullition begins at a certain temperature, which varies in different liquids, but which, for equal pressures, is always the same in the same liquid.

3. Whatever be the intensity of the source of heat, as soon as ebullition begins, the temperature of the liquid remains stationary.

The influence of pressure referred to in the first of these laws is of much greater importance here than it was in the case of the fusion of a solid. This is because of the readiness with which a gas or vapor responds to difference of pressure, and of the fact that slow evaporation passes by gradual stages into rapid evaporation, or boiling. We may generalize this statement by saying that a liquid boils when the tension of its vapor is equal to or exceeds the pressure it supports. Hence, as the pressure increases or diminishes, the tension of the vapor and, therefore, the temperature necessary for boiling must increase or diminish; it being borne in mind that the temperature of a liquid cannot be raised above its boiling-point. The close relation between boiling temperature and pressure may be shown by the experiment illustrated in Fig. 19. In a round-bottomed glass flask water is boiled for some time, and when the steam has been coming off sufficiently long to have driven out all of the air, the heat is withdrawn and the flask closed by a tight-fitting cork. It is then inverted and clamped, as shown in the figure. If the bottom is then cooled by wringing out cold water from a sponge, the water begins to boil again. The explanation is as follows: When the flask was closed and inverted, the space above the water was filled, not with air, but with vapor of water. When the upper part of the flask was cooled by the application of cold water from without, its first effect was to condense a portion of this steam. Hence the pressure upon the surface of the water was much reduced, and the water started to boil because the tension of the vapor at its surface was greater than the pressure for the time being. As soon as boiling liberates more steam the pressure becomes greater again and boiling ceases.

An important application of the fact that water and other liquids evaporate more rapidly under reduced pressure is found in the use of vacuum-pans and apparatus for concentration of liquids *in vacuo*. The third law of boiling has also important bearings. If heat is absorbed during boiling without showing any effect in the increase of temperature, it must be stored up in the vapor as potential energy, capable of being given out again in the condensation of the vapor to the liquid state.

FIG. 14.



Boiling under reduced pressure.

The analogy of these phenomena to those of the latent heat of fusion, before discussed, is seen at once, and similar deductions follow here.

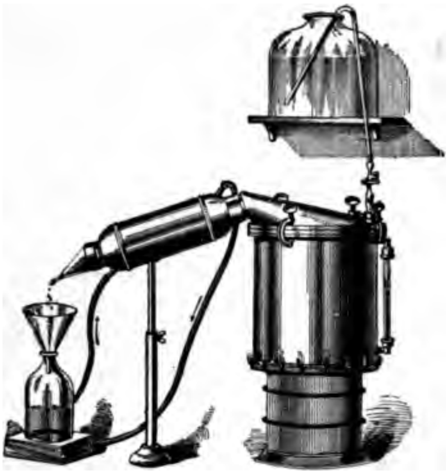
Different liquids show different values for the latent heat of evaporation. In the case of water this value is 537 degrees; that is, to convert one pound of water at 100° into steam at the same temperature requires sufficient heat to raise 537 pounds of water one degree.

The most effective forms of refrigerating apparatus now in use are those in which the rapid evaporation of volatile liquids, like ammonia and sulphur dioxide, is made to produce cold. In the modern ice-machines the evaporation of these liquids is aided by vacuum-pumps, and the gas so generated is again liquefied by the aid of condensing pumps. Solutions of brine are cooled by this rapid evaporation, and the chilled brine then circulates through coils of pipes, it may be, to long distances from the pumping machinery.

Condensation of Vapors.—This is the reverse of evaporation. It takes place whenever the temperature of the vapor drops below the boiling-point of the liquid. It may, however, be also effected by pressure or because of the chemical affinity of the vapors for some other substance. By combining the influences of cooling and pressure, the most volatile of vapors have been condensed. The so-called "permanent gases," which until within a few years resisted all efforts at condensation, have now been liquefied by combining great cold with powerful pressure. Illustrations of this will be found under Hydrogen and Oxygen.

Distillation is an operation by which, taking advantage of the volatility of a liquid, we may separate it from dissolved or admixed solids or other liquids of higher boiling point. To do this it is vaporized by heat, and this vapor, after separation from the admixed material, is condensed by itself and obtained as a more or less pure liquid. This is commonly effected in what is termed a still, a form of which is shown in Fig. 20. It consists essentially of three parts: the *body* of the still, a vessel of copper, or of copper tinned over the inside surface; the *head* or helm, which fits on the body, and from one side of which a tube goes to the *condenser* or worm, or, as in the illustration, the condenser and the head of the still may be finished in one piece. The condenser or worm consists of a tube or series of tubes around which cold water is kept flowing in order to effect the condensation of the heated vapors as they come over.

FIG. 20.



Remington still.

In this way water may be separated from the impurities, both gaseous and solid, which it contains, and the product is known as "distilled water," the purest form for chemical and pharmaceutical purposes. Alcohol or ether may be recovered from various solutions after they have been used as solvents to extract some valuable constituent from a crude drug. In manufacturing operations the same principle is utilized on an immense scale, as in petroleum refining, where fractional distillation is the means adopted to separate the various components of the mixture known as crude petroleum, and in the preparation of alcohol and alcoholic liquors from the products of fermentation.

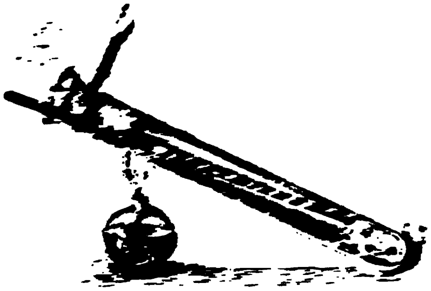
IV. TRANSMISSION OF HEAT.

Both the heat and the light vibrations travel through ether from the source of heat or light without raising the temperature of the intervening space. When they strike upon a body to which these vibrations can be communicated, it feels the effects of heat and the temperature is raised. Such heat is called *radiant* heat, and it is said to be radiated from the source of heat.

If, however, the end of a metal bar is heated, a rise of temperature is soon recognized some distance from the heated spot, and it may extend throughout the entire length of the bar. The heat is here transmitted through the particles of the metal, and the molecular vibration is not merely an instantaneous one passed on, as in the case of heat rays radiating through air or ether, but continues for some time, and shows its effect in the rise of temperature. The heat in this case is propagated by *conduction*.

[illegible] **Conduction of Heat.**—We find great differences in the ease with which bodies conduct heat. We have good conductors and bad conductors. Among solids, metals are the best conductors, while glass, resins, and wood are poor conductors. Liquids and gases are also poor conductors of heat. Both vegetable and animal tissues are poor conductors of heat. Cotton, wool, straw, and bran are all bad conductors. The relatively poor conducting power of liquids is shown in the experiment illustrated in Fig. 21. Snow may be packed in a test-tube and water put above it. On inclining the tube as shown in the cut, and applying the heat at the top of the liquid, the water may be made to boil without melting the snow. Poor conductors of heat are used both for the purpose of retaining heat and shutting it out from bodies or spaces to be kept cool. Thus, steam-pipes at all times and water-pipes in winter are packed in asbestos, magnesium carbonate, straw, felt, and other non-conducting materials, to prevent the loss of heat. Ice, on the other hand, is packed in sawdust or shavings to keep out the heat and prevent its rapid melting. Fireproof safes have the spaces between the inner and outer walls packed with non-conducting material, so that while the outer plate may be heated red-hot, the inner plate does not be-

FIG. 21.



Water a non-conductor.

come heated sufficiently to injure the books and papers that the safe may contain. Snow is a bad conductor of heat, and a layer of snow is capable of keeping the earth under it warm.

2. Radiation of Heat.—That the heat rays emanating from a source of heat are propagated through space without heating it is shown when a screen is interposed in the path of the rays. The sensation of heat at once disappears, as the surrounding air has not been heated to any notable degree by the heat rays passing through it. That radiant heat is propagated in vacuo can also be shown by experiment, and is in accordance with probability, as the radiant heat of the sun comes to us through space outside of the earth's atmosphere.

Of the laws governing the intensity of radiant heat we need only note the one that the intensity is inversely as the square of the distance. We will see later that this accords exactly with the observation of the nature of the light rays, and shows the close relationship between them. Radiant heat, when it strikes upon a body, may be reflected, diffused, absorbed, or transmitted. From polished surfaces, whether plane or curved, the heat rays are reflected or thrown back. But this reflection is never complete. Some of the rays are irregularly reflected or diffused. On the other hand, bodies which are poor reflectors absorb the heat rays in large amount. Such bodies, like lampblack, white lead, and other finely-divided substances, absorb the bulk of the rays which strike upon them. Among transparent substances, a notable difference exists in the readiness with which they transmit the heat rays. Rock-salt in transparent plates transmits the heat rays very perfectly ; alum, on the other hand, absorbs the rays and transmits very little.

3. Convection.—Liquids, as before stated and illustrated, are poor conductors of heat. When heat is applied to a liquid like water, the conductivity is so slight that, as shown in Fig. 21, ice or snow contained in the same vessel will not be melted, although the water may be brought to boiling at the top of the vessel. It is different, however, when heat is applied at the bottom of a vessel containing water or other liquid. The layer of the liquid nearest the point where the heat is applied becomes heated and at once moves upward, while a current of colder liquid moves downward to take its place. It is by these currents, which move the particles of the liquid from one place to another continuously, that the heat is mainly distributed, and not by the conductivity of the liquid. These ascending and descending currents may be

[illegible]

[illegible] OF HEAT

Steam Engines.—[illegible] ways. [illegible] mechanical [illegible] energy [illegible]

[illegible] mechanical energy [illegible] steam engines [illegible] and [illegible] mixture of gas and air.

[illegible] a piston moving [illegible] admitted [illegible] and [illegible]

Steam engines may be divided into two classes, non-condensing and [illegible] as they exhaust their [illegible] condensed [illegible] exhaust end of the [illegible] the back pressure [illegible] of an atmosphere instead [illegible] pressure, as in the non-condensing engine.

[illegible] according to the use to which they are to [illegible] engines.

[illegible] is made to drive [illegible] the explosion of a mixture of gas [illegible]

[illegible] is also used as a source [illegible] engines. A portion of the [illegible] and a second portion is [illegible] heated chamber and by its explosion drives [illegible]

CHAPTER IV.

RADIANT ENERGY.—II. Light.

I. NATURE OF LIGHT.

1. Comparison of Heat and Light.—We have already spoken of the undulations or vibrations which, radiating out from sources of light like the sun, are communicated to the ether which fills space, and are thus propagated until they strike upon bodies whose molecules are capable of taking up the vibrations and developing what we call heat energy. We saw also that chemical combination or combustion, friction, and other causes were capable of initiating these vibrations and serving as sources of heat. The sun, the great source of these heat vibrations, and most other sources of heat, are also capable of radiating undulations of a more systematic, wave-like character, which have one or both of two different effects. They may act upon the retina of the eye, and when communicated by the optic nerve may produce upon the brain the sensation of vision, or they may act upon certain chemical salts, decomposing them, because of what is called actinic power. Most generally, sources of heat become sources of light when the molecular vibration becomes more rapid, as the light undulations are more rapid and of shorter wave-length than the heat rays. Thus, a bar of metal, when heated, gives off at first only heat vibrations recognizable by the rise in temperature. After a time a red glow begins to appear and light rays of greatest length and slowest time of vibration are emitted. When the iron is still further heated it becomes white-hot, and the waves are now of shortest wave-length and quickest vibration. The range of wave-lengths for light rays is not large, and, according to the most careful calculation, varies only from .0000271 of an inch for the B line in the red of the spectrum (see p. 72) to .0000155 of an inch for the H line in the violet. Beyond the violet end of the spectrum, however, are many rays of still shorter wave-length, which do not affect the optic nerve, but have strong actinic value. The sun is the great source of radiation for all these undulations, and emits the widest variety of heat, light, and actinic rays.

A *luminous* body is one which emits light rays. Bodies may be self-luminous or original sources of light, like the sun, a candle-flame or gas-jet, and a fire-fly, or merely illuminated bodies which shine by reflected light, like the moon, and bodies lighted by ordinary daylight.

Transparent bodies are those which readily transmit the luminous rays. *Translucent* bodies transmit light less readily, so that at most the outlines of bodies can be seen through them. *Opaque* bodies do not transmit light at all, and cut off the light rays completely. Some bodies, like metals, which are opaque in bulk, become translucent or even transparent when in very thin layers. A *shadow* is the space where the light rays have been intercepted by an opaque body lying in their path.

2. Transmission, Velocity, and Intensity of Light.—In a homogeneous medium the light rays are always propagated in a straight line. This is illustrated when a beam of sunlight enters a dark room. Its path is revealed by illuminated particles of dust and shown to be in a straight line.

Light travels through space with great velocity. Accurate observations made by astronomers have allowed this velocity to be calculated with considerable exactness. It has been found to be about 186,000 miles in a second. Determinations by physical methods have confirmed these figures.

The intensity of illumination on a given surface is inversely as the square of its distance from the source of light. That is, a given unit of surface at twice the distance from the source of light of another surface will receive one-fourth the light.

Photometers are instruments for measuring the relative intensities of light. The form in common use is the Bunsen or bar photometer. It consists of a screen of paper mounted in a box which slides to and fro on a graduated bar. The paper screen has a central spot saturated with paraffine. Fixed at one end of the bar is a standard light, usually a sperm candle, of definite weight, while the light to be compared is placed at the other end of the bar. If the two lights are of equal intensity, the grease-spot does not show on the paper. When one side is more strongly illuminated the spot appears dark on that side and light on the other. It is then necessary to move the box containing the paper screen until the spot just becomes invisible. Its position on the bar is then noted, and the relative distance from the two ends taken for the calculation. The result is usually referred to a standard candle and expressed in what is called candle-power.

II. REFLECTION OF LIGHT.

We have before spoken of the path of a ray of light entering a dark room, as shown by the illuminated particles of dust, to be a straight line. If this ray strike obliquely upon a horizontally placed mirror or polished surface, we will also notice that a ray of light is thrown off or *reflected* from the mirror, and on measuring the angle made by the entering ray and the horizontal mirror, and that made by the reflected ray and the mirror, they will be found to be equal. From the experiment we may deduce the following two laws of the reflection of light:

1. The angle of reflection is equal to the angle of incidence.
2. The incident and the reflected ray are both in the same plane, which is perpendicular to the reflecting surface.

Not all of the light of the incident ray or beam is, however, reflected in this way. Unless the reflecting surface be an absolutely smooth one, some of the light is irregularly reflected or diffused. It is this which enables us to see objects. The light which falls upon a sheet of paper is scattered or diffused, so as to render it visible in all directions. If a reflecting surface were absolutely smooth, it would be invisible. We would simply see in it the image of other objects. Objects about us are thus illuminated by the diffused light reflected from the clouds, the air, and other surfaces, and so they become visible, although they may not receive the direct rays of light from the sun. There are in fact many days when, on account of clouds, our illumination comes wholly from this irregularly reflected or diffused light.

Reflection of Light from Polished Surfaces.—*Mirrors* are bodies with polished surfaces which are employed to show by reflection objects placed before them. *Images* of the objects are thus formed. The development of these in the case of plane mirrors is very simple. The rays of light coming from the object before the mirror make with the latter an angle of reflection equal to the angle of incidence, and so come to the eye. But the eye always sees objects in the direction from which the rays reach it, so that the image appears in the prolongation of the reflected ray, and at a distance back of the mirror exactly equal to that of the object from it in the other direction. The image, therefore, is not a *real* one formed by the reflected rays themselves, but an apparent or *virtual* image only. It is also a reversed image as regards right and left, as is shown when printed matter is held before a mirror. Wood-cuts and type must therefore be made in reversed position. When these are held before a mirror the image shows as a printed impression from the type will appear.

The ordinary glass mirror has in reality two reflecting surfaces, that of the glass and that of the metallic backing of the glass. Ordinarily we see only the one image, because the metallic backing is a much better reflector than the glass surface, but we can readily get the double image by placing the point of a pencil against the glass surface, when the double image allows us to judge of the thickness of the glass.

Transparent bodies the surface of which is smooth may reflect light quite regularly at times, and so form distinct images. An illustration of this is seen in the reflection of foliage and other objects in the still waters of a clear stream or pond.

All the images thus far spoken of have been formed with plane mirrors, and have been virtual images. With concave mirrors of glass or polished metal the reflected rays themselves may be made to unite to form an image, which is therefore a real image and is seen on the same side of the mirror as the object itself. This image, formed by the reflection of the rays themselves, will, however, be inverted, because the rays from different parts of the object after reflection must assume relatively reversed positions with reference to each other. The *focus* of a spherical concave mirror is a point to which the reflected rays tend to converge. If the incident rays are parallel to the axis of the spherical mirror, the focus is called the principal focus. When the object is farther from the mirror than the principal focus, the image will be inverted and real, as well as smaller than the object; when the object is between the principal focus and the mirror, the image is virtual and erect, as well as larger than the object.

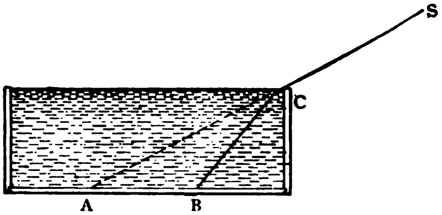
With convex mirrors we have virtual images only, appearing behind the mirror, erect and smaller than the object.

III. Refraction of Light.

1. Theory of Refraction.—When light passes obliquely from one transparent medium into another of different density, as from air to water, it is bent from its course, or *refracted.* The rule for this refraction is simply stated. When light passes from one medium into a denser medium, it is bent toward a perpendicular line; when it passes into a rarer medium it is bent away from the perpendicular line.

The phenomena of refraction may be illustrated in the experiment shown in Fig. 22. A water-tight rectangular box is constructed, of which one side is a plate of glass. Place this in a dark room and allow a slender beam of light, S, to enter in such direction that it will just pass over the edge of the box at C, making the line A, C, S. Fill the box with water and make this slightly cloudy with a few drops of an alcoholic solution of mastic or sandarac. The beam of light will now be bent at the surface of the water, and will take the direction B, C, S. As it passes from the lighter medium air into the denser medium water, it is bent toward a line perpendicular to the surface.

FIG. 22.



Refraction of light.

Numerous familiar illustrations of the phenomena of refraction may be cited. If we place a coin in the bottom of a basin in such position that it is just hidden by the edge of the basin from the observer looking obliquely from the side, and then pour water into the basin, the coin becomes visible. The reflected rays of light on emerging from the water into air are bent away from the perpendicular, and as the eye sees the object in the prolongation of the ray which reaches it, we seem to see the coin at a point on the bottom beyond its true position. If one stand in a pool of clear water, the depth of which is everywhere the same, the bottom will appear to curve upward on all sides and the water deepest just below the eye of the observer. A few feet distant, water four or five feet deep may seem not over a foot in depth. If, however, the bottom seems flat, the water would grow deeper as one walked outward from the point of observation. The danger of such a deceptive appearance is obvious.

The angle made by the incident ray of light with the perpendicular is called the *angle of incidence*; that made by the refracted ray with the perpendicular is called the *angle of refraction*. The ratio between the lines of these two angles is called the index of refraction, and varies, of course, with the media.

When light passes from a denser into a rarer medium the angle of refraction is greater than the angle of incidence. When, in such a case, the angle of refraction becomes 90°, the angle of incidence is called the *critical angle*, because when the angle of refraction becomes greater than 90° the refracted ray will not emerge, but will be reflected back again from the surface of the denser medium. This is called *total reflection*, and is more complete than the ordinary reflection of light, where, because of the imperfection of the reflecting surface, some light is always irregularly reflected or diffused. The phenomena of total reflection can be easily shown by means of a glass cube, such as is often used for a paper-weight or inkstand. Objects below the cube are invisible through the side faces, because of this total reflection. Similar effects of total reflection of the images of objects contained in aquaria are frequently observed, and add greatly to the interest of their appearance.

The mirage seen in the desert and at times at sea is an optical illusion, by which inverted images of distant objects are seen as if below the ground or in the atmosphere, and is based upon the fact of total reflection, owing to the unequal density of the several layers of the atmosphere through which the rays of light pass.

2. **Prisms and Lenses.**—A prism is any transparent refracting medium bounded by planes inclined to each other. The angle made by the two sides through which the light enters and emerges is called the angle of refraction of the prism. Both flint and crown glass are in use as materials for prisms, but the former possesses the higher refracting power. We may note two effects of prisms upon light passing through them,—

1. Light of any kind is refracted or bent out of its course.
2. White light is dispersed into a band or spectrum of colors.

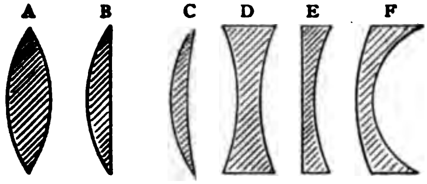
This second effect will be noted later under another heading.

Lenses are transparent media, usually of glass, which from the curvature of their surfaces have the power of causing luminous rays either to converge or diverge. The combination of spherical surfaces, either with each other or with plane surfaces, gives rise to six kinds of lenses, which are illustrated in Fig. 23. A is a *double convex*, B a *plano-convex*, C a *concavo-convex* or *converging meniscus*, D a *double concave*, E a *plano-concave*, and F a *convexo-concave* or *diverging meniscus*.

The first three, which are thicker in the centre than on the edges, are converging in their effect on rays of light; the others, which are thinner in the centre, are diverging.

A double convex lens will bring parallel rays to a point called the *principal focus*. The distance from the centre of the lens to this point is called the *focal length* of the lens. If, however, the rays reaching the lens are not parallel, but start from a point a little beyond the principal focus of the lens, they will be focussed to a point on the other side of the lens farther than the principal focus. In this case the point of origin of the rays and the point to which they are focussed constitute *conjugate foci* of the lens.

FIG. 23.



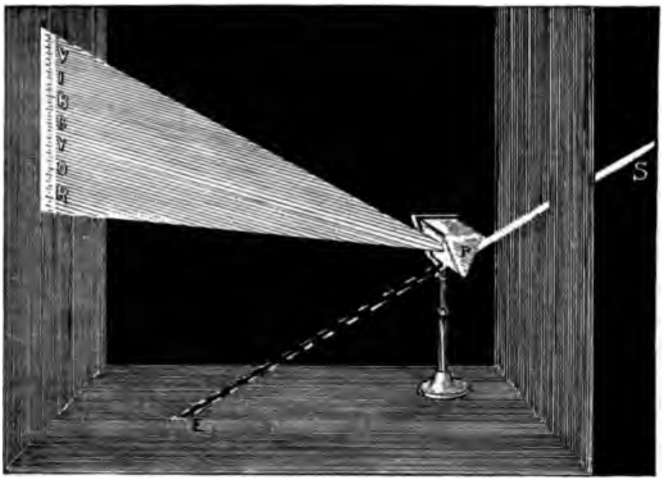
Lenses.

When the double convex lens is used to examine an object placed on the opposite side of the lens from the observer, but within the principal focal distance, an erect and magnified image of the object will be seen. This is the use we ordinarily make of a magnifying or reading lens. It constitutes the *simple microscope*. The eye and the object must in this case be in the conjugate foci of the lens for distinct vision, and as the lens is moved near the object the eye must recede. If, however, an object like a candle-flame be placed beyond the principal focus of the lens, there will be formed on the other side of the lens, and can be received on a screen, a real but inverted image of the candle-flame. If the object be so distant that the rays from it come approximately parallel, the rays will converge to a small but distinct image in the principal focus of the lens. This is shown when we use a double convex lens as a burning-glass and focus the rays of the sun to a point, which is a small but distinct image of the sun itself. With double concave lenses, which cause the rays of light to diverge, virtual images only are formed, whatever the distance of the object. They are on the same side of the lens as the object, are erect, and smaller than it.

3. Decomposition of White Light—Spectrum.—We have already referred to the fact that the effect of a prism upon a beam of light passing through it is twofold,—that, in addition to the refraction or bending from its course, white light is decomposed into a series of colored rays. The explanation of this is, that the rays which make up solar and other varieties of white light are not equally refrangible, and hence in passing through a prism they are dispersed and form a band of colors known as a *spectrum*. This is illustrated in Fig. 24.

If a beam of white light, S, be allowed to strike upon a prism, P, it is all refracted, but the component parts are refracted in different degrees, the red rays least, the orange next, and then the yellow, green, blue, indigo, and violet in the order named. The result is that, instead of a spot of white light appearing on the floor, E, a band of seven colors appears upon the wall or a screen placed at a height above the floor. This band is, in reality, a series of overlapping images of the sun, which can be again superposed by means of a double convex lens, when there will appear in the focus of the lens a white spot.

FIG. 24.



Solar spectrum.

While the colors of the solar spectrum merge imperceptibly into each other, so that many tints might be said to exist, the colors cannot be decomposed further, as when the red rays or any of the others taken singly are passed through a second prism they are uniformly refracted and give a spot of red or other color. These colors are, therefore, homogeneous, and light composed of them is known as *monochromatic* light.

The seven colors of the spectrum may be reunited to form white light in a variety of ways. If the spectrum formed by one prism be allowed to fall upon a second prism of the same material and the same refracting angle as the first, but inverted, the latter reunites the several colors and the emergent pencil is colorless. A concave mirror upon which the spectrum may be cast will also reunite the colors, and a white spot will be formed in the focus of the mirror.

The recomposition of white light from the colors of the spectrum may be shown most strikingly by the aid of Newton's disk. This is a card-board disk about a foot in diameter, on which are pasted alternate segments of colored paper in the order of the colors of the spectrum. When this is rotated rapidly, the eye receives the impression of white light, because the color impressions succeed each other upon the retina so rapidly that they are superposed, and the impression is that of white light only.

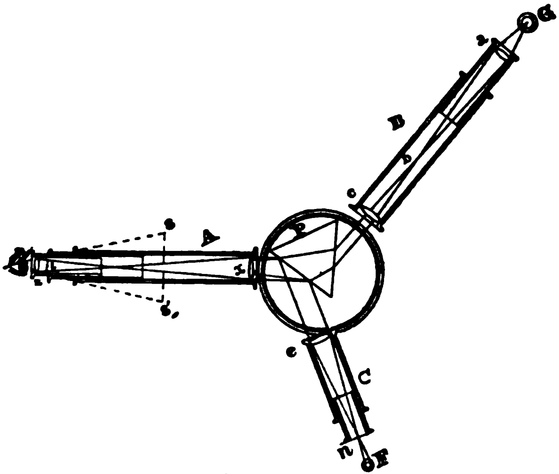
Complementary Colors.—While the combination of all the colors of the Newton's disk produces white light, we may by the combination of individual colors get numerous composite shades. Thus, if we remove the red from the set of colors, on combining the remaining colors we get a bluish-green. This is then said to be the complementary color to red, because when united with it white is produced. Similarly, purple is the complementary color to green, and an ultramarine blue to the yellow.

It must not be understood that two pigments showing such colors complementary to each other when mixed yield a white product, but that the two color impressions when superposed give the effect of white light. Thus, if chrome-yellow and ultramarine blue be mixed, the result will be a green pigment, while a yellow and a blue light combine to give us white as the resultant.

The color of bodies depends upon the manner in which they act upon white light. A portion of the rays is absorbed, and that which remains determines the color of the body. If the unabsorbed rays traverse the body, it is colored and transparent; if, on the contrary, they are reflected, the body is colored and opaque.

4. Spectrum Analysis—Spectroscope.—The examination of the light from different luminous bodies by the aid of a prism has led to important discoveries as to the nature of the light and the luminous bodies. This study has been made possible by the aid of the spectroscope first proposed by Bunsen and Kirchhoff. A sectional view of this instrument is given in Fig. 25. The rays from the source of light, G, falling upon the lens *a*, are made to converge at *b*, the principal focus of the lens *c*, so that they are thrown as parallel rays upon the prism P. After refraction, they fall upon the lens *x*, which forms a real and reversed image of the spectrum at *i*. This is magnified by the eye-piece so that a virtual image is formed at *ss'* much enlarged. The third arm of the instrument, C, is for the purpose of throwing upon the prism, and so into the observing telescope, an image of a micrometer scale which has been photographed upon glass at *n*. By its means the relative position of lines or bands seen in the spectrum can be determined.

FIG. 25.



Spectroscope.

When examined by the aid of such a spectroscope, we find that luminous bodies are capable of yielding three different kinds of spectra.

If the light from a white-hot solid or liquid body be examined, a continuous band of all the colors from red to violet will be observed. Such a spectrum is called a *continuous spectrum*. When the glowing body is in the condition of gas or vapor, we have a series of bright lines or bands against a black background. This is termed a *bright-line spectrum*. When, however, sunlight is examined by the spectroscope, the continuous spectrum appears crossed by hundreds of dark lines. The light from the fixed stars is similar, and such spectra are called *absorption spectra*. The dark lines of the solar spectrum, known as Fraunhofer's lines, were first fully explained by Bunsen and Kirchhoff, who proved that many of them corresponded to the bright lines obtained in the spectra of the vapors of such metals as sodium, calcium, iron, etc.

They therefore suggested the following explanation of the solar spectrum. The sun is probably an intensely glowing solid or liquid mass. This would give a continuous spectrum without either bright or dark lines. But the glowing mass is surrounded by an atmosphere containing cooler (although brillant) metallic vapor. This vapor would absorb light of the same kind as it emits, and hence dark lines would show in the spectrum in the same position as those occupied by the ordinary bright lines of these metallic vapors. This theory has been rendered very probable by experiments in which the bright lines of elements like sodium have been reversed and caused to appear as dark lines by passing the light from a very hot sodium flame through a cooler flame of the same vapor. We can also increase the natural absorption by causing the sun's light to pass through more sodium vapor placed in front of the spectroscope slit.

The study of the spectra of various elements, and the accurate mapping of the dark lines of the solar spectrum, show that a large number of the metals known to us on the earth occur as vapors in the sun's atmosphere.

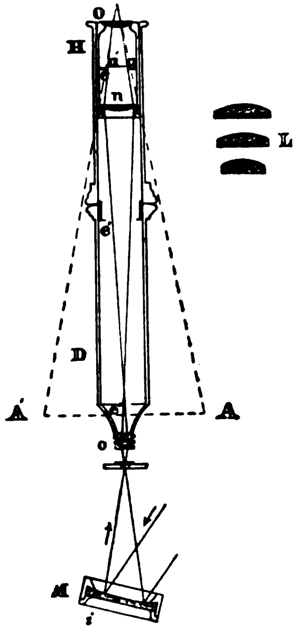
With the aid of this method of spectrum analysis chemists have discovered a number of new and relatively rare metals, such as cæsium, rubidium, thallium, indium, gallium, and scandium. It has also furnished an invaluable means of detecting impurities in chemical preparations which would otherwise escape notice.

Absorption spectra of a somewhat different character are also obtained when solutions of coloring matters like chlorophyll, hæmateïn, etc., are placed in glass cells and interposed between a source of light and the slit of the spectroscope. Broad absorption bands show, extinguishing at times the whole violet end of the spectrum.

IV. Optical Instruments based upon the Use of Lenses.

1. The Microscope.—The simple microscope, as we have seen, is merely a double convex lens of short focus, by means of which we can look at objects placed between the lens and its principal focus. The image produced is an erect and magnified virtual image of the object. In the simple microscope the measure of the linear magnification produced is the ratio of the apparent diameter of the image to that of the object, while the superficial magnification is the square of this ratio. The compound microscope consists essentially of two condensing lenses: one with extremely short focus, called the object-glass or objective, because it comes down immediately over the object; the other acts simply as a means of magnifying the image formed by the first and is called the eye-piece. The method of combining these lenses and the formation of images by means of them is illustrated in Fig. 26. In this case the objective, *o*, consists of three small condensing lenses, which together act like a single very powerful lens. The object is placed at *i*, and the rays, passing through an additional lens at *n*, inserted here to render the image achromatic, form a real and magnified image at *aa'*. This image is then magnified by the lens O and a much magnified virtual image is formed at AA'. The two lenses, *n* and O, together constitute in this case the eye-piece, just as the three small lenses, *o*, constitute the objective. The magnifying power of the compound microscope is obtained by multiplying the magnifying power of the objective by that of the eye-piece. Thus, if the magnifying power of the lens *o* is 50 diameters and that of the lens O is 4 diameters, the image seen will be magnified 200 diameters, or the superficial enlargement will be 40,000 times the natural size of the object. The degree of magnification is often determined experimentally by means of a micrometer eye-piece fitted to the microscope.

FIG. 26.



Compound microscope.

2. **The Telescope** is an instrument for viewing distant objects. In the astronomical telescope the rays come to the lens approximately parallel. They may be received upon a double convex lens and brought together in the principal focus of the lens, or upon a concave metallic mirror, in the focus of which the image is formed. The former constitutes the refracting, the latter the reflecting telescope. In the former the double convex lens, which is known as the object-glass, forms an inverted image of the heavenly body between the eye-piece and its principal focus.

The image is then magnified by the plano-convex lens serving as eye-piece. As there is no magnification except by the eye-piece, this ought to be of very short focal length. In the refracting telescope the object-glass is made as large as possible and must be achromatic,—that is, a combination of a double convex lens of crown glass with a concave lens of flint glass. In this way the dispersion of one lens is corrected by the opposite dispersion of the other, and the result is a colorless image.

The great Lick telescope in California has an object-glass thirty-six inches in diameter and a focal length of forty-seven feet, costing over $50,000, and has a magnifying power ranging from 180 to 3000 diameters. It is now exceeded in size by the Yerkes telescope belonging to the University of Chicago, which has an object-glass of forty inches aperture and a focal length of nearly sixty-four feet.

The reflecting telescope of Newton has a mirror of polished metal, or silvered glass, which receives the parallel rays. These are reflected on to a small plane mirror set in the tube at an angle of 45°, near the other end from the large mirror, and by this are thrown into an eye-piece placed in the side of the telescope. The great reflecting telescope of the Earl of Rosse has a mirror or speculum six feet in diameter.

Still another form of telescope is the Galilean, which is one of the simplest, as it consists only of a double convex lens to collect the rays and cause them to converge, and a concave lens to intercept them and form an erect, virtual, and magnified image of the distant object. This form, while no longer used for astronomical purposes, constitutes the modern opera-glass.

The terrestrial telescope, or spy-glass, differs from the astronomical telescope in having two additional condensing lenses which restore the image to the erect position, as the object-glass and eye-piece of the other forms give us an inverted image only.

3. **The Lantern and Camera.**—The projecting lantern, or stereopticon, is used for throwing magnified images on a screen in a darkened room. It consists of a closed box of wood or metal in which is placed a strong oil lamp provided with a reflector or a lime light. In the front of the box are fixed one or two plano-convex lenses which converge the light upon the lantern-slide, which is a photograph, drawing, or painting upon glass. Beyond this a double convex focussing lens is placed so that the slide shall be a little beyond its principal focus. The lens will then produce a real, inverted, and enlarged image upon a screen

placed at a suitable distance. To get the image in proper position the lantern-slide is, of course, put in an inverted position. The image on the screen will be the more magnified as the slide approaches the principal focus of the lens, which is, therefore, set so as to be moved to and fro.

In the photographic camera we have the reverse of the projecting lantern. It is a dark chamber with a convex lens in front and a screen at the back on which to form an image of objects in front of and outside of the camera. This image is real, inverted, and usually smaller than the object. It is visible to the operator back of the camera, as the screen is made of ground glass, which, when side light is shut out, is semi-transparent. In order to form a sharp image the lens is given a movement to and fro, and the screen at the rear of the camera box is also capable of a forward and backward movement by means of a rack and pinion. When a clearly defined image is obtained, a cap is put in front of the lens, the ground-glass screen is removed, and a plate-holder containing a sensitized glass plate is slipped into its place. This brings the photographic plate exactly in the position of the screen, and the image will be cast upon it. The slide in front of the plate-holder is then drawn out and the cap removed from the lens, when the reflected rays of light quickly act upon the sensitive surface.

Photographic Processes.—The plates used at present in photographic processes are of two kinds: the "wet plates," with a film of collodion carrying the sensitive salt of silver, and the "dry plates," coated with an emulsion of gelatin and bromide or chloride of silver. To prepare the former, a glass plate is carefully cleaned and then a solution of collodion impregnated with iodide of ammonium or cadmium is poured upon it and allowed to flow to and fro until the plate is uniformly coated. The plate is then immersed for about a minute in a bath of nitrate of silver containing thirty grains of the salt to an ounce of water. This latter operation, called the *sensitizing*, must be performed in a dark room. The plate is then allowed to drain and is placed in the frame for use in the camera. The dry plates are more generally used at present, because they are more sensitive than the others and can be prepared in quantity and kept, suitably preserved from light, for long periods of time.

On removing the plate from the plate-holder in the dark room after the exposure, no change is visible, but on pouring over it a *developing* solution, an image gradually appears. For developing, an alkaline solution of pyrogallic acid or a solution of ferrous sulphate and an oxalate are generally used, although many organic compounds, like hydroquinone, are also found to act as developers. When the image has been sufficiently developed, the plate is washed and the unchanged iodide or bromide of silver is dissolved away by immersion in a bath of sodium thiosulphate (hyposulphite). The plate is then again washed, and the film containing the image, now known as a *negative*, is dried and coated with a thin coating of transparent varnish. From this negative may be printed *positives* on prepared or sensitized paper, or on glass suitable for lantern slides.

4. **The Eye as an Optical Instrument.**—The human eye is a camera, and the retina the sensitive surface upon which images are constantly formed to be communicated by the optic nerve to the brain.

The outer covering of the eyeball, the *sclerotic coating*, or white of the eye, is quite firm and constitutes the frame of this camera. Inside of this is the *choroid coating*, which gives to the interior of the eye the black lining necessary for absorbing all useless or diffused rays. In front we have the transparent *cornea*, set in like a watch-crystal; the colorless and transparent *aqueous humor*, filling the space between the cornea and the *crystalline lens;* and back of this the jelly-like *vitreous humor*, filling the whole remaining cavity.

In front of the crystalline lens we have the *iris*, a diaphragm with a circular opening which can be widened or contracted at will by muscular effort, the opening constituting the *pupil* of the eye; and spread out over the rear of the cavity is the *retina*, which is the sensitive plate of the camera, and by its connection with the optic nerve conveys its impressions to the brain.

The eye, like the camera, requires to be focussed according to the varying distance of the object. This is effected mainly by a change in the curvature of the front of the lens. For instance, by a strong pressure of the ciliary muscles at either edge of the crystalline lens the curvature is increased, thus accommodating the eye for viewing near objects. When this muscular effort is relaxed, the lens again becomes flatter and is in adjustment for more distant objects. The eye is, therefore, rested by fixing it on objects at some distance. If the eye be now considered as an optical instrument, we will see that its crystalline lens, being a double convex lens, must form real and inverted images of objects placed before us. That the images formed on the retina of the eye are inverted, has been shown experimentally with the eyes of albinos, in which, on account of the absence of the choroid coating, the image is visible. That the brain is able to restore all these inverted images to the natural position without apparent effort is due mainly to training and the aid of the sense of touch, with which we have been accustomed to aid the vision from earliest infancy.

The distance of distinct vision varies greatly in different individuals. For small objects like print the normal distance is from ten to twelve inches.

Persons who see distinctly only at a short distance are called *near-sighted*, and those who see distinctly only at a long distance are called *long-sighted*. The usual cause of near-sightedness is a too great convexity of the cornea or the crystalline lens, in consequence of which the rays, instead of forming an image on the retina, are focussed at a point in front of it. The remedy is found in the use of diverging glasses, which tend to throw the focus farther back and so bring it upon the retina. The cause of long-sightedness is an insufficient convergency of the lens of the eye and consequent formation of images at a point back of the retina. With advancing age especially the crystalline tends to become flatter. The remedy is the use of converging glasses, which aid in bringing the rays to a focus exactly upon the retina.

V. POLARIZATION AND DOUBLE REFRACTION.

1. **Polarization of Light.**—According to the undulatory theory of light, the particles of ether through which a ray of light is propagated vibrate in a variety of planes perpendicular to the line of propagation. When this light is polarized, the vibrations of the ether particles take place in a single plane perpendicular to the line of propagation. The unaided eye cannot distinguish between them, but a variety of means exist by which the difference can be demonstrated.

Light may be polarized by reflection, and, in fact, most reflected rays exhibit the phenomena of plane polarization. A glass mirror which reflects the rays of light at the same time polarizes them. Light is also polarized by reflection from water, from the clouds, and all objects about us which aid in diffusing sunlight.

2. **Double Refraction.**—A large number of crystallized solids possess the property of dividing an incident ray which passes through them into two distinct rays, which are unequally refracted and form two images. This phenomenon is known as double re-

fraction. It is shown best with Iceland spar or transparent calcite. If a crystal of this mineral be placed over a page containing printed characters, each letter will appear double, and if the crystal be revolved, one set of letters will revolve around the other. The two rays which emerge from the doubly refracting crystal are known as the ordinary and the extraordinary ray, and are found to be polarized or set in a plane at right angles to each other. One of these rays may be entirely suppressed and a single polarized ray transmitted by making from a crystal of Iceland spar what is known as a Nicol's prism. A rhombohedron of calcite is sawed through from one obtuse angle to the other, and the surfaces, after being polished, are cemented together with Canada balsam. After refraction one of the rays strikes the balsam surface at an angle greater than the critical angle, and is, therefore, totally reflected, passing out at the side and leaving only the one ray to pass through the prism. Two Nicol's prisms are used together, one as a *polarizer* for light and the other as an *analyzer* to examine it. Light polarized by reflection from an inclined mirror may also be examined with a Nicol's prism as an analyzer. Plates or sections cut from the mineral tourmaline also serve for polarizing light, and a pair of these plates is often used to examine objects by polarized light.

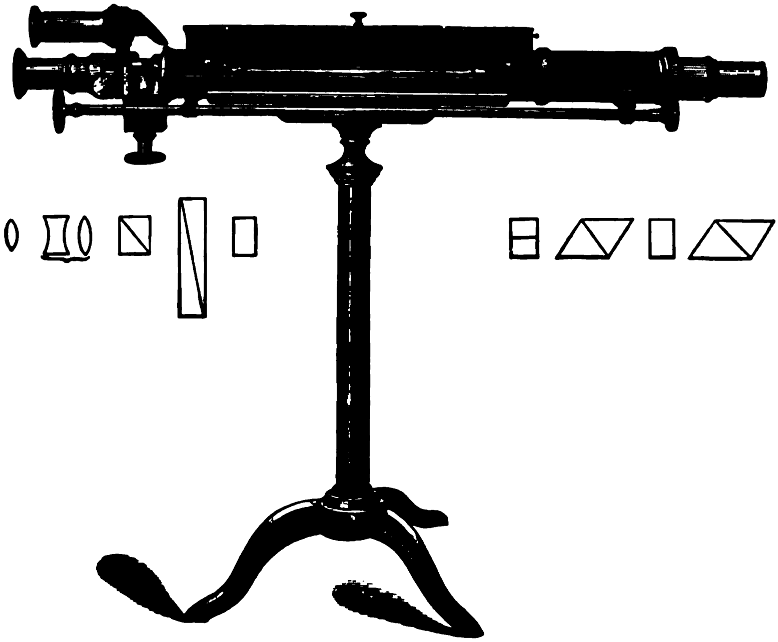
3. **Applications of Polarized Light.**—By the aid of polarized light we are able to distinguish between minerals or salts of different crystallographic systems, and determine to which a given fragment of a crystal may belong. Thin slices of the crystal in question, if examined between two Nicol's prisms or with the tourmaline plates, will show rings of color in case the crystal belong to any other than the regular system.

Those belonging to the tetragonal or hexagonal systems show circular rings on which appears a cross, which is black or white according to the position of the analyzing prism. Such crystals are called *uniaxial.* Those belonging to the orthorhombic, monoclinic, or triclinic systems show elliptical rings on which appear black or white bands or curves. Such crystals are called *biaxial.*

Beautiful colors are produced by the action of polarized light, even when the object is not definitely crystallized. Microscopes are frequently provided with a set of two Nicol's prisms, one under the stage and the other in the eye-piece, in order that the delicate structure of objects can be studied under polarized light.

Many organic substances, such as sugars, essential oils, and alkaloids, when in solution show characteristic action upon the ray of polarized light, rotating it through a circle to the right or left. The *polariscope* is an instrument based on this principle, for examining sugar solutions, and by its aid the strength or purity of all classes of saccharine products may be determined.

FIG. 27.



Polariscope.

It is shown in Fig. 27. The glass tube containing the sugar solution is shown lying in the axis of the telescope and the polarizing prisms. To the right below is shown the polarizing prism; to the left are the analyzing prism, a quartz plate, quartz wedges of opposite rotatory power, and the lenses of the telescope.

CHAPTER V.

MAGNETIC ENERGY.

I. MAGNETS, NATURAL AND ARTIFICIAL.

A CERTAIN black mineral (ferroso-ferric oxide, Fe_3O_4) was early known to possess the property of attracting iron or steel. It was known as *magnes*, from the city of Magnesia, in Asia Minor, near which it was first discovered. It was later called *lode-stone*, because of the property of leading or pointing north and south when freely suspended. Fragments of this mineral are now known as native magnets, and the property thus manifested is called magnetism. Native magnets, however, as a rule, have been replaced in experimental work by the smaller and more convenient artificial magnets of steel. Soft iron can also be magnetized, but, as we will see later, is not adapted for permanent artificial magnets, as it does not retain the power as well as steel. These magnets are commonly known by the designations bar magnets, magnetic needles, and horseshoe magnets. The latter have the convenience that because of their shape the two ends of the magnet are near each other, and can be readily covered by a piece of soft iron, known as an armature, which tends to strengthen and preserve the full magnetic power of the magnet. It is found, moreover, that in a steel magnet the magnetic effect does not penetrate very far, so that several bar or horseshoe magnets, separately magnetized and then riveted together, are more powerful than a single magnet of the same size as the compound one.

II. PROPERTIES OF MAGNETS.

The most important property possessed by the magnet, either natural or artificial, is the power of drawing to it or lifting up small pieces of iron, such as nails or tacks. Iron is not the only metal thus drawn to the magnet. Nickel and cobalt are also attracted, although in a lesser degree. This influence of the magnet is not dependent upon the presence of air, nor is it hindered by the interposition of solids, like wood or glass. The attraction takes place in vacuo and through non-magnetic solids as readily as under normal conditions.

Polarity.—A piece of iron is attracted with unequal intensity by the different parts of a magnet. The two ends possess this power in the highest degree, and the middle of the bar or horseshoe is apparently almost destitute of the power. This is seen to advantage if a bar magnet or needle is dipped into iron filings. Thick bunches of the filings will adhere at either end, while the central part of the bar is practically bare and free from filings. The ends of the magnets, or points in which the magnetic power is concentrated, are called the *poles*, and the part of the magnet which seems to be destitute of power is called the *neutral line*. Again, if a magnetic needle or bar magnet be suspended freely, we shall find that one pole will always point to the north and the other to the south. Hence we designate one as the *north pole* and the other as the *south pole* of the magnet. On bar magnets they are usually marked N and S, while on the magnetic needle the north pole is usually arrow-pointed.

III. LAWS OF MAGNETISM.

1. Attraction and Repulsion.—If the two poles marked N of two bar magnets be brought close to each other, we find no evidence of any attraction, and if, instead of two bar magnets, we take a freely suspended or oscillating magnetic needle and approach its pointed end with the north pole of a bar magnet, we find an actual repulsion,—the north pole of the needle is driven violently away while the two are yet some distance apart. If, on the other hand, the pole of a magnet marked N be approached by the pole of another magnet marked S, the two are attracted, and on touching hold together strongly. In the case of the oscillating magnetic needle, a pole of a magnet will cause the end of the needle of opposite name to swing violently toward the approaching magnet. These observations are summarized in the law of magnetic attraction : *Poles of the same name repel and poles of contrary name attract one another.*

2. Location of the Magnetic Power.—When a steel bar or needle is magnetized, even though the magnetism be effected by rubbing it with one pole of a magnet only, it acquires both north and south polarity, and if this bar be broken in two and the division continued until the pieces are quite small, the same condition exists in each of the fragments. These results are very important as giving us some idea of the nature of the magnetic influence. It undoubtedly resides in the molecules themselves, each of which must be supposed to have been given magnetic polarity when the bar or needle was magnetized. Therefore no mechanical subdivision can rob them of this property. At the same time the strong manifestation of the magnetic power at the two ends, and the existence of a neutral line for the time being in the middle of the bar, shows that the force is cumulative in either direction, and it is wanting in the middle of the bar because the forces temporarily neutralize each other there.

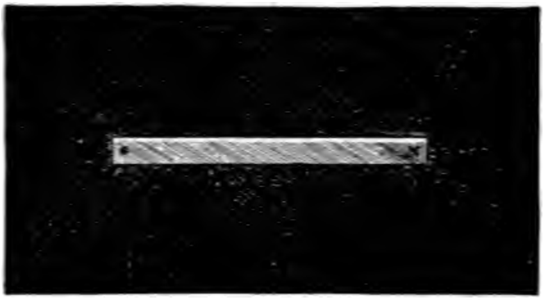
3. **Magnetic Induction.**—A piece of soft iron brought close to a strong magnet is affected by it more strongly than appears in the simple attraction. While under the influence of the original magnet it becomes a magnet itself, and is capable of attracting and repelling another piece of iron, according to the laws of magnetic attraction. This is due to what is termed *magnetic induction.* The end of the piece of iron next to the inducing magnet is given a polarity the opposite of that possessed by the pole exerting the influence, while the end of the iron farthest from the inducing magnet shows a polarity the same as that of the pole with which the iron is in contact. This induction takes place through glass or paper or other non-magnetic substance, without appreciable loss.

The influence in the case of iron is only temporary, and when detached or removed from the inducing magnet it loses its power at once. In the case of steel, on the other hand, this power is not immediately or wholly lost on detaching it from the inducing magnet. This is due to the fact that while steel has considerable magnetic retentivity, or coercive force, soft iron has very little. Hence permanent magnets are made of steel, while, as we will see later (see p. 97), electro-magnets are made of soft iron.

4. **Lines of Magnetic Force.**—If a bar magnet be laid upon a horizontal surface like a table and covered by a glass plate or a sheet of card-board, upon sifting over the glass or card-board fine iron filings we will find that they arrange themselves in peculiar curves, as illustrated in Fig. 28. These are known as the *lines of magnetic force*, and indicate the lines in which the influence of the magnet is felt. It will be noticed that they seem to radiate out from the neighborhood of the two poles, and that the curved lines from the two poles join and make a series of circles enclosing the neutral line of the magnet. These curves thus formed by the iron filings, however, do not indicate that the magnetic force is felt in narrow lines only, but they mark its direction. The entire

space around each of the poles is permeated by this influence, and is, therefore, known as the *magnetic field*. The strength

FIG. 28.



Magnetic curves.

of the attraction within this field is governed by a law of distance similar to those already noted under heat and light. It is expressed as follows: *Magnetic attraction or repulsion varies inversely as the square of the distance through which it acts.*

IV. THE EARTH AS A MAGNET.

1. The Influence of the Earth upon Magnets.—We have already seen that a magnetic needle if freely suspended will always, after oscillation, come to rest in a position pointing north and south. We will also find, if the needle be suspended so that it can swing in a vertical plane, that as we move from the equator toward the pole the needle will dip increasingly, and near the pole it assumes a vertical position. These two results we attribute to the earth's influence. We have effects analogous to these if a powerful bar magnet be laid upon a table and we hold suspended over it by a fine thread a delicate magnetic needle. The latter, as it approaches the large magnet, immediately assumes a position parallel to it, and as we proceed from the neutral line of the large magnet toward the pole the small needle dips toward the pole approached, and when immediately over it assumes a vertical position. If over the south pole of the large magnet, it is the pointed or north end of the needle which dips down, and, if over the north pole of the magnet, it is the unmarked or south end of the needle.

2. The Earth Itself a Magnet.—We are led by the analogy just stated to consider that the earth itself acts as a great magnet, and that it is to its directive influence that the oscillating needle always tends to assume the north-and-south direction. If the earth be considered to act as a magnet, we should be able to locate its poles. These *magnetic poles* of the earth were, in fact, discovered by the navigator, Sir James Ross. The north magnetic pole was found on the western coast of Boothia in 70° north latitude, and a point in the South Sea was found where the inclination or dip of the needle was 88° 37', whence the position of the south magnetic pole was calculated to be in about 75½° south latitude. It will be seen that the magnetic poles of the earth do not agree in position with the geographical poles. Hence the needle does not in most places point due north and south or in a line determined by the north star. The angle which the needle makes with the geographical meridian is known as the *angle of declination.* It is found that this angle differs at different places, and that for any one place it changes slightly from year to year. The magnetic axis of the earth, in fact, is slowly oscillating from east to west.

3. **Cause of Terrestrial Magnetism.**—The cause of the earth's magnetism is unknown. It is generally believed that it is due to electrical currents flowing from east to west, so that the earth is in effect an electro-magnet (see p. 97). These currents are undoubtedly influenced by the sun, as is shown by the coincidence of changes in the appearance of the sun and the outbreak of magnetic storms upon the earth. These latter at times disturb magnetic needles and telegraph wires over the whole world. The auroral displays seem also to be connected with these magnetic disturbances.

V. APPLICATIONS OF MAGNETISM.

Permanent magnetism has few applications compared with those that have been found for electro-magnets. These will be noticed farther on. The most important application of permanent magnets is in the *mariner's compass.* In this the freely oscillating magnetic needle is mounted in such way that under the influence of the earth's directive action it is made to indicate the direction in which a ship is moving. For this purpose one or more magnetic needles are attached to the under surface of a circular disk of card-board or mica, upon the upper surface of which are marked the thirty-two points of the compass. This disk is supported upon a delicate pivot moving in an agate cup, so that it responds to the slightest change of course of the ship.

With the general introduction of iron and steel ships the use of the compass would seem to be attended with great difficulty, because of the local attraction for the needle. It has been found possible, however, to correct for this local influence so as not to interfere with the accuracy of the directive action of the needle. The compass is supposed to have been known to the Chinese long before its introduction into Europe in the twelfth century.

Permanent magnets, as well as electro-magnets, are also used in separating magnetic iron ore from accompanying sand and crushed rock material, and in picking out small particles of scrap iron from malt and grain before crushing.

CHAPTER VI.

ELECTRICAL ENERGY.

UNDER the influence of heat, magnetism, mechanical and chemical action, as well as by the action of natural forces, a form of energy may be developed in bodies to which the name of electricity has been given. This name was first given, some six centuries before Christ, to characterize the phenomena produced by rubbing bodies like amber (Greek, ηλεκτρον), and the identity of these with the atmospheric phenomena of lightning and thunder was only established toward the close of the last century by Franklin. We shall discuss electrical energy under two main heads—the electricity of friction and the electricity of chemical action—and then note the most important of its recent applications.

A. ELECTRICITY OF FRICTION.

1. Conditions of Production.—If a stick of sealing-wax, sulphur, or hard resin be rubbed briskly with a piece of flannel, it will acquire the property of attracting light bodies, like slips of paper, feathers, pith balls, etc. A glass tube carefully dried and rubbed with a silk handkerchief will show similar phenomena. In a dark room the bodies so rubbed often appear slightly luminous, and sparks are sometimes given off when they are touched. It is evident that these are manifestations of a new form of energy developed by the friction of the two bodies and distinct from heat, which may be developed at the same time. The generally received explanation of this change of energy into a new form is that friction and the other means referred to disturb the neutral condition in which the molecules of bodies ordinarily exist, and develop therefrom two opposing influences, which then give us the so-called "electrical" phenomena. These influences may be designated as *positive* and *negative*, or *vitreous* and *resinous* electricity.

The development of electricity of either kind in a body is said to give it a certain *potential* as compared with another body, either electrified or unelectrified. A body charged with positive electricity is said to have a positive potential, while a body negatively charged has a negative potential. These opposing charges may be equal, in which case, when the two bodies are brought into contact, they neutralize each other and leave the bodies unelectrified, or they may differ in potential, in which case a residue remains of the stronger charge.

If instead of rubbing resins or glass we rub metals with flannel or silk, apparently no electrical effects are produced. This want of electrical excitement is, however, only apparent. If a metal tube is provided with a glass handle by which it may be held and is then rubbed with silk or flannel, it becomes charged with electricity. Its seeming inability to become electrified is due to the fact that it is a *conductor* of electricity, and hence the charge passes off rapidly into the hand or the object with which it was in contact. We may, therefore, distinguish two classes: *conductors*, like metals, water and aqueous solutions, plants and animals, and *non-conductors*, like silk, glass, resins, rubber, and dry air. Non-conductors are also often called insulators, as they prevent the loss or dissipation of a charge of electricity accumulated upon a conductor. Glass and hard rubber are thus used in practice. We can now somewhat understand the result attained when a stick of shellac is rubbed with a piece of flannel. Both become electrified, the shellac taking the negative charge of electricity and the flannel the positive charge. On the other hand, when glass is rubbed with silk, both likewise are electrified, but the glass takes the positive electricity and the silk the negative electricity. Both these results are, however, explained if we arrange the substances referred to consecutively in what is known as a potential series. In this list the substances are named in such order that any one becomes positively electrified when rubbed with one of the bodies following, but negatively when rubbed with one of those which precede it:

1. Cat's skin.
2. Flannel.
3. Ivory.
4. Rock-crystal.
5. Glass.
6. Cotton.
7. Silk.
8. The hand.
9. Wood.
10. Metals.
11. Caoutchouc.
12. Sealing-wax.
13. Resin.
14. Sulphur.
15. Gutta-percha.
16. Gun-cotton.

2. Laws of Electrical Attraction and Repulsion.—While we have referred to the distinction between positive and negative electricity we have not shown how this different character in electrified bodies may be ascertained. If a stick of sealing-wax be rubbed with flannel or cat's skin, and after suspending it with a silken thread it be presented to another stick of sealing-wax similarly treated, the two will repel each other. Two glass rods rubbed with a silk handkerchief will similarly repel each other, but an electrified glass rod and an electrified stick of sealing-wax or resin will attract each other. It may also be shown that when any two unlike bodies are rubbed together they both become electrified, and that when one will attract the other will repel a third electrified body. This difference of charge of course follows from a consideration of the potential series given above. Both of them will attract an unelectrified body, and by induction develop in it one or the other of the two electrical conditions.

The laws of electrical attraction and repulsion have been determined as follows:

1. Electrical charges of like name repel each other · electrical charges of opposite name attract each other.

2. The force with which each of the two charges attracts or repels the other is directly proportioned to the product of the two quantities of electricity and inversely as the square of the distance between them.

A body charged with either positive or negative electricity will exert an influence upon unelectrified bodies in the neighborhood and decompose the neutral condition existing in them, attracting to the surface next to the electrified body a charge the opposite to that which it contains. At the same time the decomposition of the neutral condition sets free both kinds of electricity, and while one is drawn toward the original electrified body, the other is driven toward the farther extremity of the body which comes under its influence. Such action is called *induction*, and by its means a body once electrified by friction is capable of exerting an influence upon surrounding bodies and developing in them corresponding charges. If this induced electricity is drawn off by suitable conductors and the body again presented in the neutral condition, fresh inductive action will develop fresh charges, and in this way notable charges of both positive and negative electricity can be accumulated. The various newer forms of frictional electrical machines are based upon the principle of repeated induction developing anew fresh electrical charges.

3. **Electrical Machines.**—In the older forms of electrical machines we have simply a circular plate or hollow cylinder of glass, which is rotated rapidly while pressing against pads of silk or leather. These latter are coated with an amalgam or with a bronze powder (stannic sulphide), and by their friction with the

glass develop electricity. The plate becomes charged with a positive electricity, which is taken off by a metallic comb and accumulates on a brass knob known as the prime conductor, while the pad which presses on the glass plate receives a negative charge which accumulates on a second insulated metallic conductor. A spark may now be taken from either of the insulated conductors. If, however, the conductor which received the negative charge be "grounded,"—that is, connected with the floor or table by a metallic chain,—the potential of the positive conductor becomes greater, and longer sparks can be taken from it. A newer and more powerful form of frictional machine is the Toepler-Holtz, which is in reality a combination of two induction machines. On the back of a stationary glass plate are two cards which act as inductors, and on a smaller revolving glass plate in front of the former are pasted a series of tin-foil carriers, each of which has in its centre a button designed to serve as a contact. A stationary metal rod crosses diagonally in front of the moving plate, and to this are attached flexible wire brushes. As the movable glass plate revolves, these brushes touch the two tin-foil carriers, which are at diagonally opposite positions on the plate, and remove the induced charges from them. As these carriers come around in front of the inductor cards they touch metallic brushes which make contact with the inductors through metallic rods and thus recharge them with positive and negative electricity respectively. The cards then act inductively upon the revolving glass plate again and communicate to it fresh quantities of the two forms of electricity to be taken up by the brushes of the diagonal rod. The metallic conductors attached to the stationary plate terminate in knobs between which a discharge of sparks is kept up while the other plate is in revolution. These conductors are provided with insulating handles of hard rubber, and are made to slide in and out of metallic sockets, so that the distance between the discharging knobs can be lengthened or shortened according as the difference of potential between the positive and negative charges becomes greater or smaller.

Condensers.—If two metallic surfaces be brought near to each other and yet be kept apart by some insulating medium, we may, by charging one with either positive or negative electricity, cause a charge of opposite name to accumulate in the other by induction. Hence such a combination is called an electrical accumulator, or condenser of electricity. The simplest form would be a pane of glass coated on either side to within an inch of the edge with sheets of tin-foil. More generally a glass jar is used, and this is coated within and without with tin-foil for about two-thirds of its height. Through a cork or wooden cap passes a metal rod terminating above in a knob and ending below in a metallic chain which is long enough to touch the inner tin-foil on the bottom of the jar. Such a jar is known as a *Leyden jar*. It may be charged by grasping it in the hand around the side and then holding the projecting knob to one of the prime conductors of the electrical machine. This charges the inner coating with that kind of electricity which had accumulated on the prime conductor, and at the same time the outer coating by induction takes a charge of the opposing kind. The jar may then be placed upon a table and the charges will remain with little loss for quite a length of time, but if contact is made between the inner and the outer coatings by a metallic conductor or through the body, the two opposing electricities at once unite and the jar is discharged.

If two such condensers are connected with the Holtz machine, one in contact with either prime conductor, the character of the discharge between the knobs of the prime conductors changes greatly. Instead of a continuous discharge of short sparks with rustling sound, we have a series of sharp discharges at short intervals, and much longer sparks are attainable by pulling out the metal rods to a little distance from each other. The electricity in this case apparently accumulates until the jars are charged, and with considerable tension or difference in potential leaps over the interval between the knobs.

4. **Electrical Discharge and its Effects.**—The effect of the spark discharge depends very much upon the nature of the body through which the discharge takes place. Its mechanical effects are seen most readily in the case of bad conductors. These are often shattered. Thus it is possible to pierce card-board or leather readily with the aid of the discharge from the Holtz nachine. A glass plate may also be pierced in this way. The lischarge of atmospheric electricity during a thunder-storm, as een in the lightning flashes, however, gives us the mechanical ffects on the grandest scale. The thunder-cloud and the earth onstitute the two parts of a huge condenser. When the differnce in potential has become sufficiently great to cause the disharge to take place through the intervening air, we have the ightning stroke which rends the tallest trees as well as buildings which stand out prominently or in exposed positions. Protection against this lightning discharge is sought in the case of tall

edifices by the use of metallic conductors, which, while insulated from the building, are connected with the ground.

The physiological effects of the spark discharge consist in sudden vibrating shocks felt in the arm or elbow when a Leyden jar is discharged through the person, and in a sharp prickling sensation felt on the knuckles or fingers when the prime conductors of a plate machine are touched. With large jars or a strong induction machine the spark discharge may be quite dangerous.

The luminous effects of a spark discharge vary with the potential of the two electricities and the medium through which the spark passes. Thus in ordinary air the spark is white and brilliant, in rarefied air it is reddish, and in vacuo it is violet. Rarefied gases, like hydrogen, nitrogen, and carbon dioxide, also cause the spark to show in different colors.

The heating effects of the spark discharge are also easily recognized The spark passed through inflammable liquids, like alcohol or ether, inflames them ; the spark will ignite ordinary illuminating gas, as is seen in many forms of domestic gas-lighting apparatus ; when the spark is passed continuously through a metallic wire, although relatively a conductor the wire still becomes heated. Magnetic effects are also observed. A steel bar or needle may be magnetized if placed inside a tube around which is coiled a wire, through which the spark discharge is made to pass. We will see later, under Voltaic Electricity, that powerful electro-magnets are made in an analogous manner.

Lastly, the chemical effects of the spark discharge are the effecting of chemical decompositions and recombinations of the elements. Thus, if the spark is passed for a time through dry ammonia gas, it is decomposed into hydrogen and nitrogen. On the other hand, the spark discharge will cause the union of hydrogen and chlorine or hydrogen and oxygen when admixed as gases. Among chemical effects must also be noticed the ozonizing of the oxygen of the air through which the discharge takes place. This is readily recognized by the odor which is always noticed in the neighborhood of the plate electrical machine. A fuller mention of this production will be found under Ozone.

B. ELECTRICITY OF CHEMICAL ACTION.

Voltaic Cells or Batteries.—The electricity hitherto [illegible] either as *static electricity*, because it remains, [illegible] upon the object charged, or electricity of *high* *tension*, because it accumulates upon neighboring conductors until a high tension or difference of potential is reached, when it is discharged by the passage of the spark. Differing from this in its manifestations, although not in identity, is the electricity of chemical action. If a strip of zinc and a strip of copper be dipped into dilute sulphuric acid and connected by means of a wire, bubbles of hydrogen will appear on the copper strip, instead of on the zinc strip, as they would were this immersed in the liquid unconnected with any other metal. The action of the dilute acid on the zinc is now in large part replaced by a different chemical action, and with this arises the development of electricity, which passes, during the continuance of the action, from the copper through the connecting wire to the zinc. This we term an *electrical current*. It is also known as *voltaic electricity*, from the Italian Volta, who first made this experiment, and the combination of metals dipping in a liquid is termed a voltaic cell. The escape of hydrogen in bubbles from the zinc plate does not entirely cease, unless its surface is thoroughly amalgamated with mercury, so that the effect of the impurities of the zinc in generating local or secondary currents is overcome.

The production of a current in this case is due simply to the chemical action which ensues whenever two dissimilar metals are moistened by the same liquid. This is very readily illustrated by putting a piece of zinc below the tongue and a silver coin upon the tongue. No sensation is felt until the metals touch at the edge or are connected by a metallic wire, but when they are brought in contact a circuit is completed and a sharp sensation is felt by the tongue and a copperas-like taste is perceptible.

The copper plate of the voltaic cell is known as the positive electrode or *anode*, and the zinc plate as the negative electrode or *cathode* of the battery, and the current passes from the positive electrode through the connecting wire to the negative electrode, and so through the liquid to its point of origin.

In the original voltaic cell the current soon becomes enfeebled because of the film of hydrogen which collects on the copper plate. This is called the polarization of the positive electrode, and, while it may be obviated to a degree by both mechanical and chemical means, it led finally to the substitution of what are termed two-liquid batteries for the original one-liquid battery.

Thus, in the Daniell cell we have copper dipping into sulphate of copper solution and zinc dipping into dilute sulphuric acid, the two liquids being separated by a porous earthenware jar. Hence, as the hydrogen separates, it acts at once on the copper sulphate, depositing copper on the positive electrode.

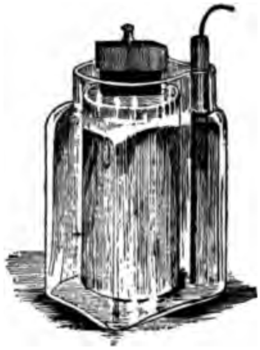
In the Grove cell we have in the outer cup zinc and dilute sulphuric acid, and in the inner porous cup platinum and nitric acid.

In the Bunsen cell we have gas carbon substituted for platinum in the inner cup, while zinc constitutes the outer element.

In the Leclanché cell, shown in Fig. 29, the inner porous cup contains a carbon plate packed in fragments of coke and powdered manganese dioxide, while the rod of zinc dips into a solution of sal ammoniac in the outer cup.

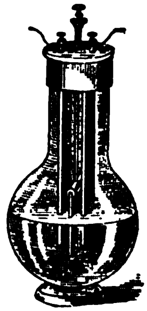
The porous cup is dispensed with in what are called "gravity" batteries, where a liquid of superior gravity is placed below and a lighter one is run in on top. Thus, in the Callaud cell we have a saturated solution of sulphate of copper below, with the copper plate resting on the bottom of the cup and connected with the circuit by an insulated wire, and above this zinc and dilute sulphuric acid, or, as it soon becomes, zinc sulphate solution.

FIG. 29.



Leclanché cell.

FIG. 30.



Bichromate cell.

Of one-liquid cells still in use, the most popular is the bichromate dipping battery, shown in Fig. 30. In this the zinc plate can be raised out of the liquid when not in use, and so the action stopped; the polarization of the positive electrode is, moreover, prevented by chemical action, as the solution is bichromate of potash acidified by sulphuric acid, and the escaping hydrogen reduces the chromic acid in the degree that it is formed. Of course, when the chromic acid is all reduced the solution has to be renewed.

A number of voltaic cells may be coupled together so as to increase the strength of the current, and then we have a voltaic battery. The coupling may be effected in two ways: each zinc may be coupled to the copper or carbon of the next cell, and so on to the end of the line, in which case the battery is said to be arranged *in series*, or the zincs may all be coupled together and the carbons all together, in which case the battery is said to be arranged *in multiple or in parallel circuit.*

2. Electrical Units.—When electricity is passing, even though it be through what we call a conductor, it meets with resistance. For purpose of comparison it is desirable to have a uniform method of measuring this. The unit of resistance is called the *ohm*, and is the resistance of a column of pure mercury, having a section of one square millimeter and a length of 106.28 centimeters, at a temperature of 0° C. For convenience, coils of wire with a known resistance in ohms are used. These are known as resistance coils and are prepared in sets, so that any resistance within quite wide limits can be measured with their aid. It is by such means that the location of a break in the ocean telegraph cables can be ascertained so that the cable may be grappled for and repaired.

The unit of current is called the *ampère.* We measure the amount of currents by noting the weight of copper that may be caused to separate from copper sulphate solution within a given time by the passage of the current. An ampère of current will deposit 0.327 milligramme of copper a second, or 1.177 grammes per hour. The current is also often measured by the amount of hydrogen and oxygen liberated within a given time by the electrolysis of water (see p. 97).

The ampère-meter is an instrument the dial face of which is graduated in ampères, while a needle deflected by the passage of the current through coils of wire moves over the scale and indicates the strength of the current.

The pressure or difference of potential which causes the electricity generated in a battery or cell to overcome the resistance of the circuit and so effect its passage is called its electro-motive force. The unit of electro-motive force is called the *volt.* It is the pressure required to maintain a current of one ampère through a resistance of an ohm. Electrometers are used for measuring difference of potential or electro-motive force.

The relation of these three units is concisely expressed in Ohm's law: *The strength of the current is equal to the electro-motive force divided by the resistance.*

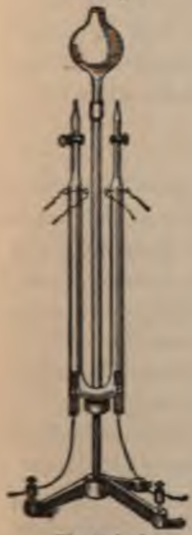
The units ohm, ampère, and volt were named in honor of the three great electricians, Ohm, Ampère, and Volta.

3. **Effects of Current Electricity.**—The main distinctions between the frictional current or discharge and the current developed by voltaic action are in tension or difference of potential and in amount of the current. Frictional electricity is of high tension but small in total amount, while the voltaic current is of low tension but greater in amount as measured in ampères. Hence the effects will differ somewhat. The mechanical effects of voltaic electricity are very slight as compared with those of frictional electricity. The physiological effects are also, as a rule, very much milder than those of the spark discharge. The wires from a voltaic battery of a dozen cells may be held in the hands without appreciable shock, but a tingling sensation is felt from very strong currents, and prolonged contact with the wires has an exciting effect upon the nerves. The heating effects are dependent, of course, upon the resistance which the circuit offers to the passage of the current and to the amount of current passing. With good conductors like copper, of sufficient section, the heating effect is slight; with wires of insufficient section, or with poor conductors, like platinum, iron, or German silver, the resistance becomes relatively great and the wire becomes strongly heated. It is thus possible, with relatively moderate currents, to fuse a thin platinum wire which may be interposed in the circuit. The luminous effects of voltaic electricity are obtained under two distinct conditions: First, when two wires from the electrodes of a battery are brought together, thus closing the circuit, a spark is seen at the point of contact, often of great brilliancy. This is also seen on breaking the circuit. Secondly, the resistance offered to the passage of the current through a poor conductor often heats the latter to such a degree that it becomes luminous. Both of these methods of obtaining luminous effects, we will see later (see pp. 101, 102), are practically applied in electric lighting.

The chemical effects of the battery current are notably more important than are those of frictional electricity, because the greater amount of electricity and the duration of the current in the first case make possible effects not to be attained in the other case. Thus the current passed through acidified water, as shown in Fig. 31, will decompose it into its constituents, hydrogen and oxygen gases, by a process termed *electrolysis*. Similar results are obtained with solutions of many chemical salts. This will be more fully treated of later under the electro-deposition of the metals, or electro-metallurgy (see p. 102).

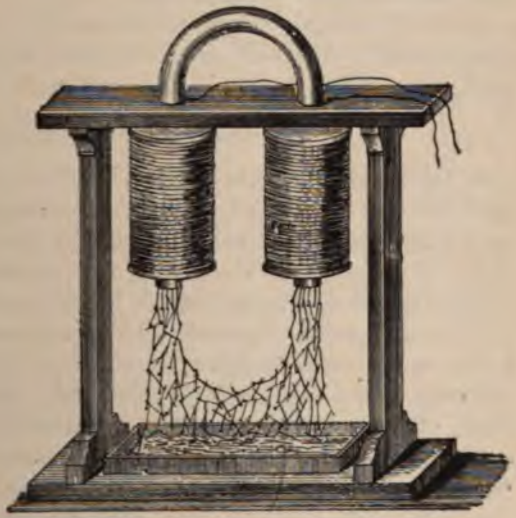
4. **Electro-Magnetism.**—The magnetic effects of the voltaic current are so important that they require special consideration. If a bar of soft iron is held at right angles to a wire carrying a current of electricity, we will find that it acquires for the time being magnetic properties. If the wire be coiled around the bar, the magnetic effect will be increased in proportion to the number of coils. To make a powerful horse-shoe magnet, therefore, it is only necessary to take two short bars of soft iron joined at one end by a cross-piece of similar metal, surround these bars by coils or bobbins of insulated wire, and pass a current through the coils. While the current passes we have, as shown in Fig. 32, a powerful magnet, but, as soft iron has little or no coercive force, the moment the current ceases the magnetism of the iron cores disappears. The coils should be wound or connected so that the current passes around one coil in one direction and around the other in the opposite direction, in order that one shall form a north pole and the other a south pole. Electro-magnets are used in almost all forms of practical electrical apparatus.

FIG. 31.



Electrolysis.

FIG. 32.



Electro-magnet.

5. **Voltaic Induction.**—We have already spoken of the in-

ducing action of a body charged with frictional electricity upon neutral bodies. This is sometimes called electro-static induction. In the case of voltaic electricity similar phenomena are very readily produced. If a magnet is moved near a wire, a current of electricity will be produced in the wire ; if an electro-magnet have a current sent through its coils, a current will be produced in neighboring wires or coils. Such currents are called induced or secondary currents. They differ in many important respects from the primary currents which may be used to incite them. The chief difference is in the relation of electro-motive force or tension to volume of current. As before stated, the primary voltaic current is of low tension but relatively large volume. The secondary or induced current is more like the frictional electrical discharge, of high electro-motive force but relatively small volume. We shall refer in the next section to the practical application of this change in character of the voltaic current.

C. APPLICATIONS OF ELECTRICITY.

1. Of Electro-Magnetism.—The first and most important application of the principles of electro-magnetism is the ***magnetic telegraph***, which was proposed in practical form by Prof. Morse in 1837. The Morse telegraph apparatus consists in the main of an electro-magnet, which, when a current passes through its coils, attracts an armature. An operator can cause this armature to move, even though many miles away, by simply sending a current over a wire leading to the station containing the apparatus. The essential instruments are the *key*, by means of which the sender controls the current and can establish or break contact by a pressure of the finger, and the *sounder*, or receiving instrument, which contains the electro-magnet, the movements of whose armature cause a clicking sound. Sometimes, instead of the sounder, a *register* is substituted, in which case the armature causes marks to be made upon a long paper ribbon or tape. The alphabet of the Morse system consists of a series of dots and dashes upon the tape or of longer or shorter clicks as heard by the sounder. A *relay* or additional electro-magnet connected with a local battery is generally inserted in the case of long circuits, so as to strengthen the current and enable it to be transmitted. The wire at either end of the line is "grounded," so that the earth is made to act as return conductor, and thus a second wire is dispensed with.

Electric bells also involve an application of the electro-magnet.

In this case the armature of an electro-magnet is so arranged that when it is drawn forward the projecting end strikes the bell. We may have either a single-stroke bell, or, as is more generally used, a bell in which the striking is kept up continuously as long as the contact is kept up by a push-button at the end of the wire which connects with the electro-magnet.

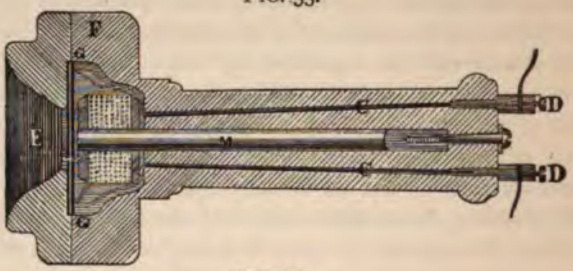
Electric clocks consist of a dial upon which two hands move by mechanism which is regulated by impulses due to the attraction and release of the armature of an electro-magnet. A number of these clocks can be regulated by one standard clock, with which the widely separated individual clocks are connected in electrical circuit. As contact is made by the attraction of the armature of the regulating electro-magnet, each large hand moves one-sixtieth of the space, marking minutes.

2. Of Voltaic Induction.—One of the first and most direct applications of voltaic induction is found in the *induction coil*, or, as it is often called, the Ruhmkorff coil. It consists of a hollow cylinder in which is a bar of soft iron with two coils of wire around it. The first of these is of relatively coarse wire connected with the poles of a battery, the current of which is alternately opened and closed, and the other of much finer wire for the secondary or induced current. Whenever the primary current is opened or closed a current passes in the secondary coil, and, as this interruption of the primary current is made very rapid and continuous, a succession of induced currents is made to pass. The effectiveness of this induction coil increases with the length of wire in the secondary coil. Fifty and sixty miles of very fine wire have been frequently used. In such cases the induced current of high electro-motive force may give rise to sparks several inches in length. Mention was made before of discharge of frictional or high-tension electricity through rarefied gases (see p. 92). With the spark from the Ruhmkorff coil this discharge through tubes containing rarefied gas is very brilliant. Such tubes are known as *Geissler tubes*, and, besides being filled with rarefied gases, are often made in part of uranium glass, which fluoresces beautifully when illuminated by the electric spark.

The telephone is a much more practical application of the principles of induction. By its means speech may be transmitted through long distances by the intervention of a magnet and induced currents in a coil of wire surrounding the magnet. The essential parts of the Bell telephone can be seen in Fig. 33.

Enclosed in the case, F, is a magnet, M, having at one end a coil of very fine wire, and a diaphragm of very thin sheet-iron, GG, which is placed close in front of the magnet. The coil of wire connects by the two wires CC with binding screws, DD, at the other end of the instrument. When a person speaks into the mouthpiece, E, the diaphragm of thin metal vibrates immediately before the magnet and causes changes in the lines of magnetic force and so electric currents in the coil which surrounds it. These currents passing over the line affect the strength of the magnet in a corresponding instrument at the other end, and in turn cause the diaphragm in front of it to vibrate, producing sound waves which will perfectly correspond with those generated by the person speaking. The Bell telephone may therefore serve either as a "receiver" or a "transmitter." The carbon-button transmitter of Edison and Blake is, however, commonly used with the Bell telephone receiver.

FIG. 33.



Telephone.

The dynamo-electrical machine is, however, the most important of all electrical apparatus. We have already (see p. 98) stated that if a magnet is moved near a wire, a current will be generated in the coil of wire, because the lines of magnetic force are cut. This, of course, may be stated another way,—if a coil of wire is moved in the neighborhood of a magnet, an electric current is generated in the wire. The common dynamo is simply a series of coils of wire with soft iron core, known as the "armature," revolving between the poles of a powerful electro-magnet known as the "field magnet," because producing the magnetic field in which the armature revolves. At the start some slight residual magnetism remaining in the core of the field magnet develops feeble currents in the coil of the revolving armature. These are carried through the coil of the electro-magnet, increasing promptly its power as a magnet, and this again acts upon the coils of the armature. A small fraction of the current developed in the rapidly revolving armature suffices to feed the field magnet, and the current then passes off through what is known as the "commutator" and collecting brushes into the conducting wires. We have produced in this way what is known as a continuous current. By dispensing with the commutator, and taking the current directly from the armature, we get alternating currents. The alternating current dynamo has some advantages over a continuous current dynamo, as the electro-motive force of this current may be raised or lowered as desired, which is not possible with continuous currents. It is claimed that the dynamo is capable of transforming over ninety per cent. of the mechanical power applied to it into electrical energy.

Electric motors do not differ essentially from dynamo machines; in fact, the action of the dynamo may be reversed and it may be used as an electric motor; the rapid rotation of its armature may be communicated to various small machines.

3. **Change of Electrical Energy into Heat.**—We have already referred to the heating effect of the voltaic current. The heat generated by the powerful currents of the dynamo machine, when passing through poor conductors or encountering electrical resistance in any way, is correspondingly greater. Two effects of this heating may be noticed: *Electrical furnaces* for carrying out metallurgical operations which require an intense heat, as in the Cowles furnace for the production of aluminum by the reduction of its oxide by charcoal, and *electric welding*, in which case two pieces of metal are welded together by bringing them in contact and passing a powerful electric current through the juncture. Iron, steel, brass, and copper may be welded in this way with great success.

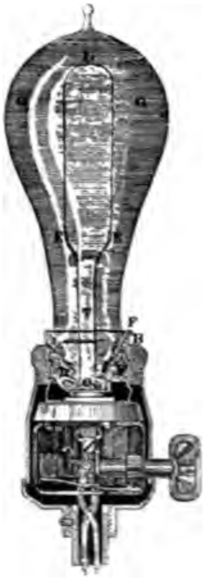
4. **Change of Electrical Energy into Light.**—The heating effect of powerful currents may be utilized for lighting purposes in one of two ways. If the two electrodes of the current from a powerful battery or dynamo be brought to within a short distance of each other, a brilliant arc light is formed, spanning the interval between the two terminals. The ends of the wires are raised to a white heat, and most metals melt or volatilize in consequence. If, however, the terminals consist of pencils of hard carbon, which is infusible, we have the brilliant white light known as the *arc light*. The carbon, of course, burns away gradually, and provision must be made for keeping the distance between the

two pencils constant, which is done automatically by a suitable mechanism attached to the lamp.

The current is also utilized for lighting effects in a still simpler way. This is to interpose at some point in the circuit a conductor of such resisting power that the passage of the current renders it white-hot. This is effected in the ***incandescent lamp***, and the substance utilized here is likewise carbon. An extremely fine filament of carbon is enclosed in an exhausted glass globe, as shown in Fig. 34, which illustrates the Edison lamp. This filament or horse-shoe of carbonized bamboo is connected at either end by fine platinum wires, which are fused into the glass and pass through, connecting with the brass fitting of the socket into which the lamp is screwed.

Arc lamps require a very high electro-motive force, usually from 1000 to 3000 volts. Incandescent lamps, on the other hand, require only 50 to 120 volts. The one current is likely to be fatal to life if by accident a naked wire is touched, the other is not.

FIG. 34.



Edison incandescent lamp.

5. Change of Electrical Energy into Chemical Action.—We have before referred to the effect of the current in electrolysis. This is practically applied in the electro-deposition of such metals as copper, nickel, gold, and silver. In all these cases the metal is deposited at the cathode or negative pole. If an article to be plated with one of the metals just referred to be hung from the negative pole, dipping into the appropriate salt solution, a plate of the metal in question is made the positive pole. As the metal separates at one pole of the current, corresponding amounts are dissolved from the plate which constitutes the other, so that the solution is kept of constant strength. If the current remain constant the deposit will be evenly made. Great use is made of electrolytic copper, as it is termed, in the manufacture of electrical apparatus, as such copper has more uniform resistance than copper obtained by smelting the ores. Nickel-plating, silver-plating, and electro-gilding are also extensively carried on.

Secondary or storage batteries are applications of this change of electrical energy into chemical action, as when the secondary battery is charged by a dynamo, it is simply put into condition for a prolonged chemical reaction, which will develop as it proceeds a certain amount of electricity, just as a primary cell or battery is capable of doing. When this reaction is complete, it will generate no further current, but a dynamo current applied to it is capable of reversing the chemical reaction just completed, and so charging it afresh for development of electricity. The batteries are made of plates of lead cast in a framework of bars crossing each other at right angles. The spaces between the bars are filled with a paste, which for the positive plate is made of red lead and sulphuric acid, and for the negative plate of litharge and sulphuric acid. When the battery is charged with the dynamo current, peroxide of lead is formed at the positive pole and spongy metallic lead at the negative pole. It is the difference in potential between the two immersed in dilute sulphuric acid that gives us the current. As the battery is discharged sulphate of lead is formed at both poles, and at the end of the discharge they are practically the same. The dynamo current is then again applied, producing peroxide of lead and spongy lead, as before.

PART II.

CHEMISTRY OF THE NON-METALS.

PART II.

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CHAPTER I.

PRELIMINARY THEORETICAL CONSIDERATIONS.

I. ATOMS AND ELEMENTAL MOLECULES.

1. **Elemental and Compound Molecules.**—We have already stated in considering the nature of matter (see p. 14) that the union of like atoms gives simple or elementary matter, of which chemists have distinguished some seventy kinds, while the union of unlike atoms gives compound matter, the varieties of which are almost endless. Obviously, it is of prime importance to the chemist to be able to distinguish with certainty whether a newly-observed form of matter is simple or compound. This can be done by submitting it to the influence of what are called *reagents*, such as strong acids and alkalies, or at times to the influence of physical agencies alone, such as heat and the electrical current. If, under these circumstances, two or more different kinds of matter result from the decomposition of the substance investigated, we had compound matter or compound molecules to start with. But if the effect of both physical and chemical agents is to leave us with the one form of matter originally taken, or a simple derivative of it due to the reagent used, we have had simple matter or a chemical element, as it is called, to deal with. Thus, salt if decomposed by electrolysis will yield sodium and chlorine, or treated with sulphuric acid as a reagent will yield sodium sulphate and hydrochloric acid, both results going to show that salt is a compound molecule containing sodium and chlorine. Silver, on the other hand, remains unchanged by physical agencies, and if acted upon by nitric acid, yields silver nitrate as sole product, thus proving its elemental character.

2. **Chemical Elements or Elemental Molecules.**—By applying the various methods of analysis to the different forms of matter found in nature, chemists have come to a knowledge

of some seventy kinds of simple matter or elemental molecules. This number, of course, is not a fixed or final one. Additional elements may be discovered, or it may be found that some of our supposed simple forms of matter are in reality compounds of other known elements.

Both the elemental molecules and the atoms which unite to form them have the same name. These names, given as the elements were discovered, in most cases have been chosen to indicate some characteristic property or to indicate the locality or country in which they were first found, although occasionally fanciful names exist. They have all been made Latin words, so that as far as possible they could be used in common by all nationalities. In the case of a few of the metals which have long been known, the common English names in current use do not agree with the Latin names. These are indicated in the following table of elements, the Latin names from which the symbols are taken being placed in parentheses.

TABLE OF ELEMENTS.

Element.	Discoverer.	Date.	Element.	Discoverer.	Date.
Aluminum	*Wöhler*	1827	Indium	*Reich & Richter*	1863
Antimony (*Stibium*)	*Valentine*	1460	Iodine	*Courtois*	1812
Arsenic	*Schroeder*	1694	Iron (*Ferrum*)	*Ancients.*	
Barium	*Davy*	1808	Iridium	*Tennant*	1804
Beryllium	*Vauquelin*	1797	Lanthanum	*Mosander*	1839
Bismuth	*Agricola*	1530	Lead (*Plumbum*)	*Ancients.*	
Boron	*Davy*	1808	Lithium	*Arfvedson*	1817
Bromine	*Balard*	1826	Magnesium	*Davy*	1808
Cadmium	*Stromeyer*	1817	Manganese	*Gahn*	1774
Cæsium	*Bunsen*	1860	Mercury (*Hydrargyrum*)	*Ancients.*	
Calcium	*Davy*	1808	Molybdenum	*Hjelm*	1782
Carbon	*Ancients.*		Nickel	*Cronstedt*	1751
Cerium	*Berzelius & Hisinger*	1803	Nitrogen	*Rutherford*	1772
Chlorine	*Scheele*	1774	Osmium	*Tennant*	1804
Chromium	*Vauquelin*	1797	Oxygen	*Priestley*	1774
Cobalt	*Brandt*	1735	Palladium	*Wollaston*	1804
Columbium	*Hatchett*	1801	Phosphorus	*Brandt*	1669
Copper (*Cuprum*)	*Ancients.*		Platinum	*Wood*	1741
Didymium	*Mosander*	1841	Potassium (*Kalium*)	*Davy*	1807
Erbium	*Mosander*	1843	Rhodium	*Wollaston*	1804
Fluorine	*Moissan*	1886	Rubidium	*Bunsen*	1860
Gallium	*De Boisbaudran*	1875	Ruthenium	*Claus*	1845
Germanium	*Winkler*	1885	Samarium	*De Boisbaudran*	1879
Gold (*Aurum*)	*Ancients.*		Scandium	*Nilson*	1879
Hydrogen	*Cavendish*	1766	Selenium	*Berzelius*	1817

Element.	Discoverer.	Date
Silicon	*Berzelius*	1823
Silver (*Argentum*)	*Ancients.*	
Sodium (*Natrium*)	*Davy*	1807
Strontium	*Davy*	1808
Sulphur	*Ancients.*	
Tantalum	*Ekeberg*	1802
Tellurium	*Klaproth*	1798
Terbium	*Mosander*	1843
Thallium	*Crookes*	1861
Thorium	*Berzelius*	1828
Tin (*Stannum*)	*Ancients.*	
Titanium	*Klaproth*	1795
Tungsten (*Wolfram*)	*De Luyart*	1783
Uranium	*Klaproth*	1789
Vanadium	*Sefstroem*	1830
Ytterbium	*Marignac*	1872
Yttrium	*Wöhler*	1843
Zinc	*Paracelsus*	15—
Zirconium	*Berzelius*	1824

3. Number of Atoms in Elemental Molecules.—The terms molecular weight and atomic weight, and the methods of their experimental determination, will be more fully explained later. It is obvious that if the weight of an elemental molecule be divided by the weight of the elemental atom contained in it, the number of such atoms that the molecule contains will be obtained. Most of the elemental molecules examined in this way prove to be diatomic; that is, contain two atoms. The exceptions so far ascertained are,—

Monatomic.	Triatomic.	Tetratomic.	Hexatomic.
Mercury.	Oxygen (in the form of ozone).	Phosphorus.	Sulphur (at about 550° C.).
Cadmium.	Selenium (below 800° C.).	Arsenic.	
Zinc.			
Barium.			

4. Properties of Atoms.

a. Atomic Weight or Mass.—We do not know, nor is it likely that we shall ever be able to determine experimentally, the absolute weight of either atoms or molecules. The numbers which we assign to the atoms therefore are not absolute but relative. The weight with which the hydrogen atom enters into chemical combination, being less than that of any other element, is chosen as the standard, and the other atomic weights are based upon this as unity. The relative atomic weights of the elements were supposed according to Prout's law to be whole numbers, multiples of unity, but the most accurate determinations now accepted give many numbers carrying fractions as the correct atomic weights. To determine the atomic weight of an element we must know its relation to hydrogen. Where it forms a compound with hydrogen, analysis of this compound will give us the ratio of weight between the element and hydrogen. If a single atom of each element be present in the compound, as in hydrogen chloride,

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CHEMISTRY OF THE NON-METALS.

oxygen develops its variation. The same thing holds true of sulphur and of nitrogen.

5. Use of Atomic Symbols.—An abbreviated form of expression rendered necessary by the constant use of the names of the chemical elements was proposed in 1815 by Berzelius, and is now in universal use. It consists in taking the first letter of the Latin name of the element, or the initial and a second letter suggestive of the name. Thus, H stands for hydrogen, O for oxygen, Cl for chlorine, K for potassium (kalium), and C for carbon. For a full list of the symbols see the table in Appendix.

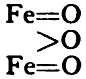
Each symbol stands for one atom of the element in question. It has also come to represent a definite amount, viz., the atomic mass or weight of the element.

Using these symbols, it becomes easy to indicate the grouping of atoms to form molecules, both elemental and compound, and the multiplication of atoms or of molecules. Thus, the molecule of ordinary oxygen, before referred to as diatomic, is written O_2, while that of ozone (see p. 166) is written O_3. The molecule of water, or hydrogen oxide, is written H_2O, in which case the numeral $_2$ following the H applies to it and it alone. The multiplication of a molecule may be indicated by the use of the same numeral placed to the right below, but outside of a parenthesis. Thus, $(H_2O)_2$ means two molecules of hydrogen oxide. Sometimes the same thing is indicated by the use of a large numeral placed before the symbols representing the molecule, as $2H_2O$. In this case a parenthesis is unnecessary, as the large 2 multiplies the entire molecule following and not merely the single symbol.

6. Graphic Symbols for Valence.—When it is desired to indicate the valence of an element, a Roman numeral is placed to the right above, thus: S^{II} or S^{IV}. These valence marks are not used ordinarily in writing formulas or expressing reactions between chemical substances, but only in so-called graphic formulas. Lines are sometimes used to indicate the linking of atoms to each other. These are known as *bonds*. Thus, H--O--H or H—O—H may be used as the graphic representation of hydrogen oxide, or it may be written $\begin{matrix}\mathrm{H}{-}\,{-}\\ \mathrm{H}{-}\,{-}\end{matrix}\!\mathrm{O}$ or $\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\!>\!\mathrm{O}$.

II. Compound Molecules.

We have already stated that the union of unlike atoms gives compound matter or compound molecules. Two cases may arise in their formation. The atoms composing them may be *directly* united, and, as there can be but two kinds of atoms in this case, such molecules are called *binary;* or the atoms may be indirectly united to each other, and, as such molecules will contain three or more kinds of atoms, they are called *ternary*.

1. **Binary Molecules.**—These, as just stated, contain but two kinds of atoms, as in the case of common salt, which contains an atom of sodium combined with an atom of chlorine, and in ferric oxide, which contains two atoms of iron combined with three atoms of oxygen. The whole number of atoms present is not limited, but they must be directly united according to their valence. This is shown by writing the compounds just mentioned with the aid of graphic formulas. Na—Cl represents the molecule of salt and  $\begin{array}{l} \mathrm{Fe{=}O} \\ \quad >\mathrm{O} \\ \mathrm{Fe{=}O} \end{array}$ that of ferric oxide.

Binary molecules are named by placing the name of the positive element first and then the name of the negative element, the termination of which is changed to *ide*. Thus, sodium and chlorine form sodium chloride, hydrogen and oxygen form hydrogen oxide. The name of the positive element remains unchanged, except where because of its variation in valence it enters into combination with the negative element in two or more ratios. In this case the positive element may take the termination *ous* or *ic*, according as it shows the lower or the higher valence. Thus, we have ferrous oxide and ferric oxide, stannous chloride and stannic chloride.

In a few cases the variation in valence is such that more than these two designations are required. We are able to extend the list sufficiently by the use of the prefixes *hypo*, meaning "under," and *per*, meaning "beyond." The first of these is applied to the word ending in *ous* and the second to the word ending in *ic*. Thus, we have four oxides of chlorine,—viz., hypochlorous oxide, chlorous oxide, chloric oxide, and perchloric oxide. Similarly the oxides of sulphur are hyposulphurous oxide, sulphurous oxide, and sulphuric oxide.

As the application of these changes to the name of the positive element has been irregular at times, the use of numeral prefixes has also been taken for the purpose of exactly indicating the composition of the molecule. Thus, carbon monoxide and carbon dioxide are generally used instead of carbonous oxide and carbonic oxide.

The combination of chemical symbols to express the composition of a molecule is called a *formula*. The formulas of binary molecules are obtained by placing the symbols of the constituents one after the other, the positive first. Thus, NaCl stands for sodium chloride, KBr for potassium bromide, MgO for magnesium oxide.

In forming binary molecules and writing their formulas it is important to bear in mind that atoms do not exist in the free state, but must come from other molecules, whether elemental or compound. It is therefore an exchange or replacement that takes place when a binary molecule is to be formed. This replacement, moreover, must always follow the laws of valence. Thus, sodium chloride, NaCl, may be considered as formed from the sodium molecule (Na_2) and the chlorine molecule (Cl_2) by interchange of atoms, or we may form it from hydrogen chloride, HCl, by the replacement of an H atom by an equivalent Na atom. In the formation of zinc chloride, $ZnCl_2$, we would replace two hydrogen atoms of 2HCl by the dyad atom Zn, and so on, according to the valence of the replacing atom.

It is sometimes convenient to consider unsaturated groups of atoms as acting together like units in the formation of compound molecules. Thus, if we withdraw an H atom from the formula H_2O, we have an unsaturated residue (OH) with the valence one, which is often taken as uniting with other atoms or groups to form saturated compound molecules. This unsaturated group or *compound radical* $(OH)^{I}$ is called *hydroxyl*. Similar compound radicals are the groups $(PO)^{III}$ called *phosphoryl*, $(CO)^{II}$ *carbonyl*, $(SO_2)^{II}$ *sulphuryl*, $(NO_2)^{I}$ *nitroxyl*, $(H_2N)^{I}$ *amidogen*, and $(CN)^{I}$ *cyanogen*. Compound radicals with an uneven valence cannot exist in a free state, but may unite with a similar group to form a molecule as like atoms unite to form elemental molecules. On the other hand, compound radicals with an even valence, like CO and SO_2, may exist in a free state, but still tend to take up other atoms or groups and become saturated.

2. Ternary Molecules.—The indirect linking of the atoms in ternary molecules involves the idea of one of the atoms acting as intermediary or standing between the others, which are held together in the molecule only by the aid of this linking atom. It is obvious from their definition that the linking atom must be of higher valence than one. In practice we have only two classes to note: first, those in which the linking atom is a dyad; and, second, those in which the linking atom is a triad.

Of the dyad elements, oxygen and sulphur are the only ones to form compounds of importance, and in by far the larger number of cases the element oxygen is the linking element. The ternary molecules in which oxygen acts in this way may be divided into three classes according to the nature of the atoms thus joined together, viz., *acids*, *bases*, and *salts*. To distinguish the acids and salts thus formed from another class of acids and salts to be referred to shortly, they are sometimes called oxyacids and oxysalts.

The general formula of a ternary acid (oxyacid), then, is $\overset{-}{R}—O—H$, in which $\overset{-}{R}$ stands for an electro-negative atom or group of atoms.

The general formula of a base is $\overset{+}{R}—O—H$, in which $\overset{+}{R}$ stands for an electro-positive atom or group of atoms.

The general formula of a ternary salt (oxysalt) is $\overset{+}{R}—O—\overset{-}{R}$, in which a positive atom or group is united by the aid of oxygen to an electro-negative atom or group of atoms.

As a molecule of water may be written H—O—H, these three classes of compounds may be considered as derived from water by the replacement of one of its H atoms by either positive or negative elements in the case of the base or acid respectively, or of both H atoms in the case of the salt, one by positive and the other by negative atoms. Hence these three classes of compounds are often said to be formed on the *water type*. They are also called acid, basic, and neutral *hydrates* respectively.

Besides the ternary acids, we have also the class of *haloid acids*. These are binary molecules in which the halogen elements (Cl, Br, I, and F) unite with hydrogen to form acid gases.

The term *acid*, in its broadest sense, may then be defined as *a compound of hydrogen with an electro-negative element or group of elements*. This definition will include the haloid acids and the oxyacids.

Besides the ternary salts, we have also the class of *haloid salts*. These are binary molecules in which the hydrogen elements are directly united with electro-positive elements or metals to form neutral salts.

A *salt*, therefore, may be defined as *an electro-positive atom or group of atoms combined with an electro-negative atom or group*.

The definition of a *base* follows from the general formula $\overset{+}{R}—O—H$, given before.

Sulpho-acids, bases, and salts are also [illegible] plays the linking part, corresponding to ternary acids, bases, and salts.

Of the triad elements which have a linking function, nitrogen, phosphorus, and arsenic may be mentioned. Only the molecules containing nitrogen need be noted. They form three classes, corresponding to the acids, bases, and salts of the water type. These nitrogen-containing molecules may all be referred to the type of H_3N (ammonia), and are sometimes referred to as *derived ammonias*. The three classes are known as *amides*, *amines*, and *alkalamides* respectively. They will be referred to more fully under Organic Chemistry.

3. **Method of Formation of Ternary Molecules.**—We have, for the sake of showing the difference of constitution, thus far referred to acids, bases, and salts as built upon the water type. We must not suppose, however, that they are always or even generally derived from water by the replacement of hydrogen atoms. They may be formed by the union of two binary molecules, as when calcium oxide and carbon dioxide unite to form calcium carbonate, a positive oxide and a negative oxide uniting in this case to form a ternary salt. Similarly, calcium oxide may unite with hydrogen oxide to form calcium hydrate, a positive oxide and water uniting to form a basic hydrate; or sulphur dioxide may unite with hydrogen oxide to form sulphurous acid, a negative oxide and water uniting to form an acid hydrate or oxyacid.

Still more frequent is, however, the formation of ternary molecules by substitution. Thus, the hydrogen of an acid is readily replaceable by its equivalent amount of a metal, and the result is a salt; or if the hydrogen of a base is replaced by a negative atom or group of atoms, the result is also a salt. Or starting with the salt, by the displacement or withdrawal of its positive atom an acid may result, hydrogen going into the place of the metal; if its negative group be withdrawn by the attraction of a strong base, the salt may be changed into a basic hydrate. In illustration of these several changes we may take the change from sulphuric acid to zinc sulphate by displacement of hydrogen by zinc, the change from calcium hydrate to calcium carbonate by the introduction of the negative carbonyl group in the place of hydrogen, the change from potassium nitrate to hydrogen nitrate (nitric acid) by the withdrawal of the potassium while hydrogen takes its place, and the change from copper sulphate to copper hydrate on the addition of an alkali.

4. Notation and Nomenclature of Ternary Molecules.—The notation of ternary molecules, like that of binaries, is based upon the valence of the component atoms. This is, of course, modified by the replacement of atoms by other atoms or atomic groups, but a graphic formula showing the linking of the atoms by bonds should be possible in all cases. This will be shown later by our illustrations.

The nomenclature of ternary molecules follows simple rules. Acids, bases, and salts are all named from their constituent atoms. The positive element, as in the case of binaries, comes first, and is not changed except to indicate its variation in valence. The termination of the negative element is changed and differs from that found in binaries to indicate the fact that it is not directly united, as was the case in the binary molecule. The negative terminations are always *ate* and *ite*. The naming of acids, bases, and salts will be considered separately.

a. Acids.—These, it will be remembered, are negative hydrates. They all contain hydrogen linked by oxygen to an electro-negative atom or group of atoms. Two methods of naming are in use. They may be called by the same names as the corresponding negative oxides, from which they are supposed to have been formed by the addition of water, merely substituting the name acid for that of oxide, as sulphuric acid from sulphuric oxide, nitrous acid from nitrous oxide, and hypochlorous acid from hypochlorous oxide; or they may be considered as hydrogen salts of the acids and so named. Thus, sulphuric acid is sometimes called hydrogen sulphate, nitrous acid hydrogen nitrite, and hypochlorous acid hydrogen hypochlorite. In this case it will be noted that to the termination *ic*, characteristic of the binary, corresponds the termination *ate* of the ternary, and to the termination *ous* corresponds the termination *ite*.

As stated, acids contain a negative atom or group of atoms linked by oxygen to hydrogen. When the negative atom itself is so linked, the number of atoms of oxygen and hydrogen (or hydroxyl groups OH) corresponds exactly to its valence. Such acids are sometimes called *ortho-acids*. Thus, in the list of oxy-acids of chlorine we would have $Cl^{VII}(OH)_7$ orthoperchloric acid, $Cl^{V}(OH)_5$ orthochloric acid, $Cl^{III}(OH)_3$ orthochlorous acid, and $Cl(OH)$ orthohypochlorous acid. It has been found, however, that such compounds containing a number of OH groups linked to one negative atom are unstable and tend to split off one or more molecules of water, leaving a modification of the original ortho-acid. Such derived acids are termed ***meta-acids.*** It is obvious, on examining the formula of such an acid as orthoperchloric acid given above, that the loss of one molecule of water will mean the breaking up of two hydroxyl groups and the leaving of one atom of oxygen in their place. This is thus expressed, $Cl^{VII}O(OH)_5$. The withdrawal of a second molecule of water will give us $Cl^{VII}O_2(OH)_3$, and of a third molecule of water $Cl^{VII}O_3.OH$. All of these acids are perchloric acids, and all would be called meta-acids. Most of the common acids are of this class, representing the more stable compounds, the full ortho-acid being in most cases unstable. Thus, $S^{VI}O_2.(OH)_2$ is the formula of common sulphuric acid, $N^{V}O_2.OH$ is the formula of common nitric acid, and $C^{IV}O.(OH)_2$ is the formula of carbonic acid. In the case of phosphoric acid two of these meta-acids are readily obtainable, $P^{V}O.(OH)_3$ and $P^{V}O_2.OH$, the first being the more stable.

It has been stated that the acid is changed into a salt by the replacement of its hydrogen atoms by metal. As in the case of the oxyacids this hydrogen must be linked to the negative atom or group by the aid of oxygen, the number of OH (hydroxyl) groups is the measure of the amount of metal that can be introduced. We term this the ***basicity*** of an acid,—that is, its base-neutralizing power. This basicity, therefore, depends upon the number of hydroxyl groups contained. Thus, $SO_2.(OH)_2$ is dibasic, $NO_2.OH$ is monobasic, $CO(OH)_2$ is dibasic, $PO(OH)_3$ is tribasic, and $PO_2.OH$ is monobasic. These common acids are all meta-acids; in all ortho-acids the basicity is of course equal to the valence of the negative atom.

b. Bases.—These are positive hydrates, containing hydrogen linked by oxygen to an electro-positive element. They are usually named by giving the name of the positive atom followed simply by the term hydrate, as potassium hydrate, KOH, calcium hydrate, $Ca(OH)_2$, ferrous hydrate, $Fe(OH)_2$, and ferric hydrate, $Fe_2(OH)_6$. These are all what may be termed ortho-bases. Few meta-bases are known, as it is only when the number of OH groups is large that they tend to form. Thus, from $Fe_2(OH)_6$ we obtain by the loss of water successively $Fe_2O(OH)_4$ and $Fe_2O_2(OH)_2$, which latter then passes into Fe_2O_3, which is ferric oxide.

The number of OH groups here determines also the saturating power of the base, which is called the *acidity* of the base. Thus, K.OH is mon-acid, $Ca(OH)_2$, di-acid, etc.

c. Salts.—These are formed by the union of acids and bases, or by replacing the hydrogen of an acid by metal and the hydrogen of a basic hydrate by a negative group of atoms.

A salt is named by placing the name of the positive atom first and then that of the negative group, ending in either *ate* or *ite*, according as the acid or acid-forming oxide ended in *ic* or *ous*. Thus, from sodium oxide and nitric acid is formed sodium nitrate, and from potassium hydrate and hypochlorous acid is formed potassium hypochlorite.

In considering the formulas of salts, we must bear in mind the basicity of the acid and the valence of the positive atom. Thus, if we have a monad metal like sodium and a monobasic acid like nitric acid they will exactly balance, and sodium nitrate, $NaNO_3$, is the result. If with a dyad metal like calcium we unite nitric acid, we must take two molecules of the latter to form the salt $Ca(NO_3)_2$. Similarly, if we take sodium and a dibasic acid like sulphuric, we must take two atoms of the metal to neutralize one molecule of the acid and form the salt Na_2SO_4. In general, to form a neutral salt such number of atoms of metal and molecules of acid must be taken as will furnish exactly the same number of bonds. If a lesser number of atoms of metal be taken than demanded by the basicity of the acid, the salt will still partake somewhat of the character of an acid; if the acidity of the base be not completely satisfied by acid, the salt will have something of the character of a base. Hence we distinguish three classes of salts: *normal* (or neutral) *salts*, in which the base and acid exactly counterbalance each other; *acid salts*, in which the hydrogen of the acid is not completely replaced by metal; and *basic salts*, in which the hydrogen of the base is not completely replaced by acid-forming groups. Thus, Na_2SO_4 is neutral sodium sulphate, while $NaHSO_4$ is acid sodium sulphate; HNa_2PO_4 and H_2NaPO_4 are both acid salts, while Na_3PO_4 is a neutral salt; $Ca(NO_3)_2$ is neutral calcium nitrate, while $Ca(OH)NO_3$ is basic calcium nitrate.

III. LAWS OF COMBINATION BY WEIGHT AND VOLUME.

1. Relation of Molecules and Volumes.—According to the law of Avogadro, equal volumes of all substances in the gaseous state contain the same number of molecules, and therefore, as a consequence, the molecules of all substances when in the gaseous state are of the same size. We are thus able to compare equal volumes of gaseous bodies just as if we were comparing single molecules of the respective substances. In this way we can experimentally determine the relative molecular weights, taking the weight of the hydrogen molecule as standard.

2. **Laws of Combination by Weight.**—We owe to the English chemist John Dalton two important laws, that of combination in constant proportions and that of combination in multiple proportions. According to the first, *each element combines with the others in a fixed and definite proportion by weight*, and according to the second, *when two elements unite in several different proportions these are simple multiples of each other.* Based upon these two laws we have the atomic hypothesis of Dalton, which furnishes the explanation of these relations.

3. **Laws of Combination by Volume.**—The French chemist Gay-Lussac has stated these relations also in two laws. According to the first, *the ratio in which gases combine by volume is always a simple one*, and according to the second, *the volume of the gaseous product obtained in a combination bears a simple ratio to the volumes of its constituents.*

These laws of combination by volume are illustrated in the formation of certain typical hydrogen compounds.

One volume of hydrogen and one volume of chlorine combine to form two volumes of hydrogen chloride.

$$\boxed{H_2} + \boxed{Cl_2} = \boxed{HCl}\boxed{HCl}$$

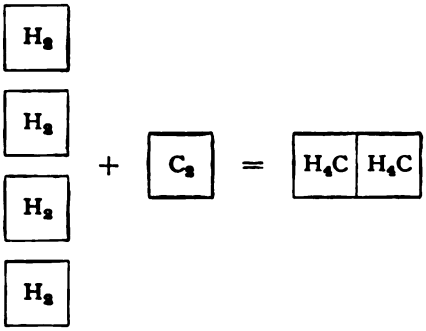
Two volumes of hydrogen and one volume of oxygen combine to form two volumes of water vapor.

$$\begin{array}{c}\boxed{H_2}\\ \boxed{H_2}\end{array} + \boxed{O_2} = \boxed{H_2O}\boxed{H_2O}$$

Three volumes of hydrogen and one volume of nitrogen combine to form two volumes of ammonia.

$$\begin{array}{c}\boxed{H_2}\\ \boxed{H_2}\\ \boxed{H_2}\end{array} + \boxed{N_2} = \boxed{H_3N}\boxed{H_3N}$$

Four volumes of hydrogen and one volume of carbon vapor combine to form two volumes of methane.



4. **Relation of Density to Molecular Weight.**—As stated, atomic weights are relative numbers based on the weight of the hydrogen atom as unity. Molecular weights are obtained by adding together the weights of the constituent atoms in a molecule. Thus, the hydrogen molecule containing two atoms would weigh 2, and as the molecule of hydrogen chloride containing one hydrogen atom and one chlorine atom weighs 1 + 35.5 or 36.5, the weights of the two molecules are as 36.5 to 2 or as 18.25 to 1. Hence the rule usually given, that the density of any body in the state of gas is half the molecular weight. Conversely it is possible by experimentally determining the density of any gaseous body to arrive at its molecular weight.

IV. CHEMICAL REACTIONS AND EQUATIONS.

1. **Meaning of Reactions and their Expression in Equations.**—A *reaction* is a chemical change taking place within a molecule or between two or more molecules. The several substances taking part in the change are called *reagents*. Moreover, as each molecule concerned has its proper chemical formula, we can state the reaction by the use of these formulas. If the several reagents taking part in the reaction are placed together connected by the sign plus and made equal to the several compounds which result also connected by the sign plus, we have a *chemical equation*. In this case the substances entering into the reaction are called the *factors*, and the substances issuing from the reaction are called the *products*.

Moreover, as every atom has its proper atomic weight, which is not altered through all the changes and rearrangement in new molecules, the chemical equation must be capable of change into a numerical equation in which both sides must sum up alike.

2. **Conditions favoring Reactions.**—As we have learned in considering the several states of matter, the molecules are freer to move, and so come into the sphere of action, when in the liquid or gaseous state than when solid. Hence fusion or solution of solids and vaporization of liquids are steps which facilitate chemical reaction. In many cases the mixing of two solids produces no reaction, but the same solids will react if fused together, or, if soluble in the same menstruum, when their solutions are admixed.

Two other points should be noted as favoring chemical change. If two substances are taken in solution and then mixed, a product may form which is insoluble in the menstruum employed. This is called a *precipitate*. If such precipitate can form by the rearrangement of the molecules taken in any case, we have an immediate formation and the reaction goes on to completion. Again, the reaction of two substances may cause the liberation of a gas. In such case the reaction is a ready one and proceeds steadily to completion.

3. **Classification of Reactions.**—The simplest kind of reaction is that which simply represents the breaking up of a complex molecule into simpler ones. Such change is frequently brought about by heat. Thus, calcium carbonate under the influence of heat breaks up into calcium oxide and carbon dioxide, thus expressed, $CaCO_3 = CaO + CO_2$, or potassium chlorate is decomposed into potassium chloride and oxygen, $2KClO_3 = 2KCl + (O_2)_3$.

The reverse of this is found when two simple molecules unite to form a more complex one. Thus, hydrogen and chlorine unite to form hydrogen chloride, $H_2 + Cl_2 = 2HCl$, or calcium oxide unites with water to form calcium hydrate, $CaO + H_2O = Ca(OH)_2$.

The great majority of reactions, however, involve two factors which by their reaction yield two products, an interchange of atoms taking place. In such cases it must be remembered that this interchange must be according to the laws of valency, and each atom or group of atoms transferred from one molecule to another must be replaced by its exact equivalent.

Thus, silver nitrate and sodium chloride when in solution react with each other to produce silver chloride and sodium nitrate, $AgNO_3 + NaCl = AgCl + NaNO_3$. Again, sodium chloride and sulphuric acid react to form sodium sulphate and hydrogen chloride, $2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$.

4. Calculations from Equations.—As before stated, every atomic symbol stands for a definite amount of an element known as its atomic weight. Hence every molecular formula stands for a definite molecular weight, and every chemical equation is capable of translation into numbers.

This makes it possible to calculate readily a variety of numerical relations both from molecular formulas and from chemical equations. Thus, the percentage composition of any chemical compound is readily calculated from its formula. If m represents the molecular weight, a the weight of any constituent atom, n the number of atoms of this constituent, and x its percentage amount, we have the proportion $m : an :: 100 : x$. This expression by the well-known "rule of three" will enable us to ascertain the values of m, a, n, or x, the other terms being known.

The most generally required calculations, however, are those of quantities entering into or produced in chemical reactions. For these the molecular weights of the factors and the products of a reaction are needed. Thus, if we take the reaction $2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3$, and put it into figures, it becomes $170 + 98 = 142 + 126$. It now becomes possible to calculate how much sodium sulphate or how much nitric acid can be produced from a given weight of sodium nitrate, or how much sulphuric acid it will take to decompose a given weight of sodium nitrate. Thus, $170 : 126 :: 100 : 74.12$ shows that 100 parts by weight of sodium nitrate will yield about 74.12 parts by weight of nitric acid. It is equally obvious that if the reaction be well understood it is possible for the experimenter to ascertain by calculation how much of any factor is needed to furnish a definite amount of a product.

CHAPTER II.

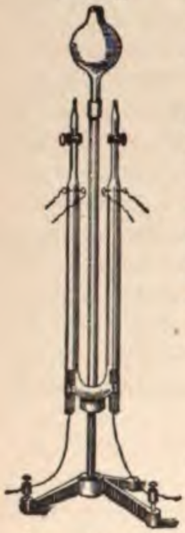
HYDROGEN.

Symbol, H. *Atomic Weight*, 1. *Valence*, I.

History. — In the sixteenth century, Paracelsus observed hydrogen while experimenting on iron with acids. Cavendish, in 1766, first investigated it, and gave it the name "inflammable air." Lavoisier, some years later, proposed the name hydrogen, which has met with general acceptance.

Occurrence.—Hydrogen occurs, in the free state, in certain volcanic gases, in the carnallite of the Stassfurt mines, occluded in meteoric iron, and in the natural gas of the Pennsylvania oil regions. In combination, hydrogen forms one-ninth of the water of the globe, and is a constituent of nearly all organic matter.

FIG. 35.



Preparation of hydrogen by decomposition of water.

Preparation.—(1) By the decomposition of water with the electric current. An apparatus like that shown in Fig. 35 is very convenient. One part sulphuric acid to one hundred parts of water assists the process by making the latter a better conductor of electricity. The products of the action are two volumes of hydrogen and one volume of oxygen, according to the following:

$$2H_2O = 2H_2 + O_2.$$

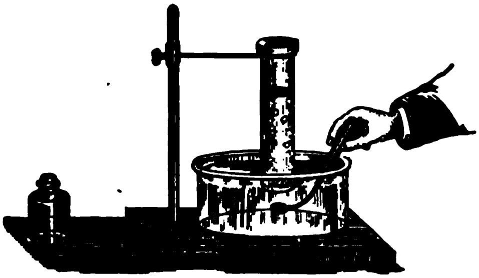
(2) By the decomposition of water with sodium or potassium. When a small piece of potassium is thrown on water, chemical action takes place at once, the metal melts, and floats around, enveloped in a flame of hydrogen, which ignites spontaneously from the heat of the action. The flame is of a violet color, imparted by the volatilization of some of the metal.

Sodium does not react so strongly with the water as to cause ignition of the escaping hydrogen, unless it be held in one spot by placing it on a piece of filter paper, when sufficient heat is developed to ignite the gas, which, in this case, burns with a yellow flame. The metal rapidly disappears in the excess of water, forming a strongly alkaline solution:

$$\underset{\text{Sodium.}}{Na_2} + \underset{\text{Water.}}{2H_2O} = \underset{\substack{\text{Sodium}\\\text{Hydrate.}}}{2NaOH} + \underset{\text{Hydrogen.}}{H_2}.$$

The gas may be collected, when sodium is used, by enclosing the metal tightly in a wire cage, and thrusting this quickly under an inverted cylinder filled with water as shown in Fig. 36.

FIG. 36.



Decomposition of water by sodium.

(3) The decomposition of water by certain metals at a red heat:

$$\underset{\text{Water.}}{4H_2O} + \underset{\text{Iron.}}{3Fe} = \underset{\substack{\text{Ferroso-ferric}\\\text{Oxide.}}}{Fe_3O_4} + \underset{\text{Hydrogen.}}{4H_2}.$$

This reaction may be carried out by passing the vapor of water through an iron tube in which some iron wire has been placed, and the whole heated to redness; the metal combines with the oxygen of the vapor, forming ferroso-ferric oxide, while the hydrogen passes out, and may be collected over water.

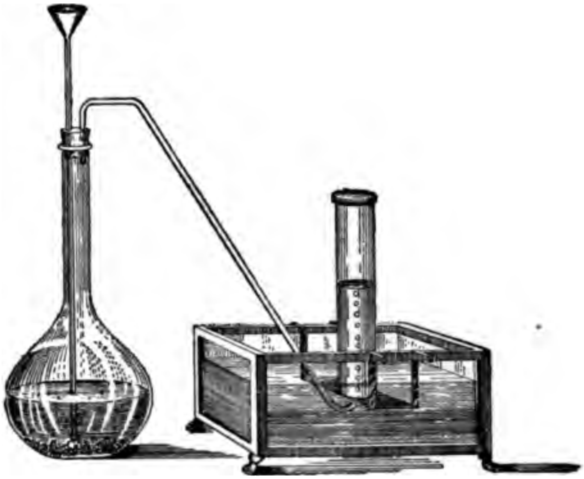
(4) By the action of dilute acids on certain metals we obtain hydrogen, as follows:

$$\underset{\text{Zinc.}}{Zn} + \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{H_2SO_4} = \underset{\substack{\text{Zinc}\\\text{Sulphate.}}}{ZnSO_4} + \underset{\text{Hydrogen.}}{H_2}.$$

Iron may be used in place of the zinc, or sulphuric acid may be substituted by hydrochloric acid, with similar results. Iron, however, does not yield as pure a gas as zinc, on account of certain carbon impurities contained in it.

The above reaction progresses satisfactorily only in the presence of water, which dissolves the zinc sulphate formed, and prevents its collecting on the metal and retarding the further action of the acid. When chemically pure zinc is used the action at first is very slow, but by the addition of a drop or two of platinic chloride solution a galvanic action is established, which causes a rapid evolution of the gas. This is the method usually employed for preparing the gas for experimental purposes, and an apparatus similar to that represented in Fig. 37 will be found convenient.

FIG. 37.



Preparation of hydrogen.

The mistake is often made by beginners of attempting to ignite the gas as it escapes from the generator; this should never be done until after one has become thoroughly familiar with the properties of the element. Explosions frequently occur by neglecting this precaution.

(5) When strong solutions of the alkaline hydrates are brought in contact with certain metals, hydrogen is evolved; in some cases, like the following, it is necessary to apply heat:

$$\underset{\text{Zinc.}}{Zn} + \underset{\text{Sodium Hydrate}}{2NaOH} = \underset{\text{Sodium Zincate.}}{Zn(ONa)_2} + \underset{\text{Hydrogen.}}{H_2}.$$

With magnesium and aluminum the action takes place at the ordinary temperature.

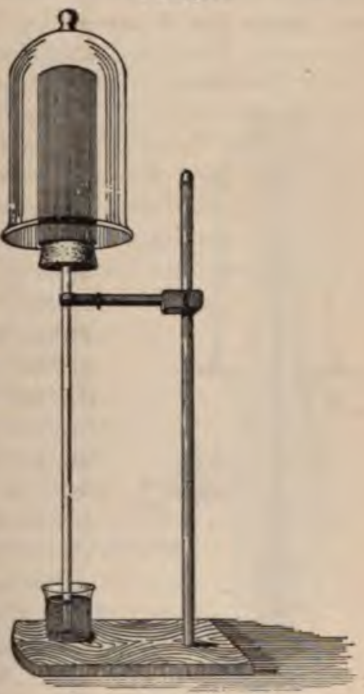
All the foregoing processes yield a gas more or less impure. In order to obtain perfectly pure hydrogen, it should be passed through a solution of lead acetate, to remove hydrogen sulphide; through a solution of silver sulphate, to remove hydrogen phosphide and arsenide; through potassium hydrate solution, to remove free acid; and, finally, over calcium oxide or phosphoric oxide, to remove moisture.

Physical Properties.—When purified as above, hydrogen is without color, odor, or taste; it is the lightest known substance; one liter weighs 0.089578 gramme at 0° and under 760 millimeters' pressure, indicating a specific gravity of .0693 when air equals 1.000, or in the proportion of 1 to 14.43. It may, therefore, be collected by "upward displacement," by simply holding a receiver over a tube from which the gas is escaping; this method, however, is unnecessary, as the gas is so insoluble in water that it is usually collected over that liquid.

Between the temperatures of 0° and 20°, it requires 50 volumes of water to dissolve one volume of hydrogen. Hydrogen may be inhaled for a short time without injurious effects, but it causes a peculiar change in the voice. Sound travels nearly four times more rapidly in hydrogen than in air, and light is refracted more strongly by it than by any other gas.

The diffusibility of hydrogen is one of its most prominent characters. This property may be illustrated by an apparatus shown in Fig. 38, in which a porous battery cell securely fastened by a rubber cork on the end of a glass tube forms the diaphragm. The lower, open end of the tube is placed in water colored with aniline or indigo, and a jar full of the gas lowered around the cell, when, as the hydrogen diffuses into the cell faster than the air comes out, the latter is driven out below, and is seen bubbling up through the water; as soon as this action ceases the jar is removed, and the hydrogen now rapidly passes out through the cell, causing a partial vacuum,

FIG. 38.



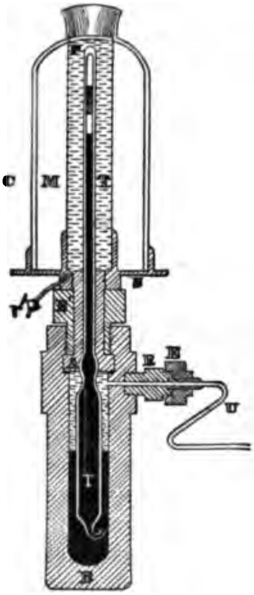
Diffusion of hydrogen.

which the water rises to fill. Since the relative diffusibility of two gases is inversely as the square roots of their densities, we have (when hydrogen equals 1) $\sqrt{14.43} : \sqrt{1}$ or 3.8 : 1; that is, hydrogen will diffuse 3.8 times more rapidly than air.

Hydrogen may be converted, by a pressure of 13.3 atmospheres and a temperature of —240°, into a steel-blue liquid, and on suddenly releasing this pressure, the vaporization of the liquid is so rapid that the intense cold thus produced converts a portion of the escaping liquid into solid particles, which almost instantly disappear. This liquefaction of hydrogen, which broke down the old distinction of permanent gases, was accomplished independently and almost at the same time by two physicists,—Cailletet, of Paris, and Pictet, of Geneva.

The apparatus of Cailletet is illustrated in Fig. 39. The pure dry gas is collected in the tube T, the lower end of which is placed in a strong cylinder containing mercury, while the upper and smaller end is surrounded by a freezing mixture. Pressure is applied to the surface of the mercury by means of a powerful hydraulic pump, through the tube U, until 200 atmospheres are obtained; this is then increased to 300 atmospheres by means of a wheel with a steel plunger. At this stage the pressure is suddenly released, when the tube containing the hydrogen becomes filled with an opaque vapor. Pictet, with more elaborate cooling apparatus, by which he produced a temperature of —140°, and a pressure of 650 atmospheres, obtained by generating the gas in a very strong retort by heating a mixture of pure potassium hydrate and formate, succeeded in obtaining the element in a solid state.

FIG. 39.



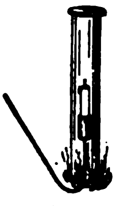
Liquefaction of hydrogen.

Hydrogen possesses the peculiar property of permeating certain metals, like iron, palladium, and platinum, at a red heat. This fact depends on the property, named by Graham *occlusion*, which some metals, especially palladium, possess, of absorbing hydrogen. For instance, platinum at 100° absorbs 0.76 volume, and at a red heat 3.8 volumes of the gas; while palladium absorbs 376 volumes at ordinary temperatures, 643 volumes at 90°, and 526 volumes at 245°. The amount absorbed depends somewhat on the physical condition of the metal, palladium deposited by electrolysis absorbing 982 volumes at 100°.

Chemical Properties.—Under ordinary conditions hydrogen has but little affinity for other substances, but at elevated temperatures or in the nascent state its behavior is quite the reverse, and we find it combines readily with oxygen; that is, burns when ignited, the product being water. The glass tube from a hydrogen generator may be converted into a jet for illustrating this property, by fusing into the end of it a small roll of platinum made from a piece of the foil. When one is sure that all the air has been expelled from the apparatus this jet may be lighted, and the gas will burn with a pale blue flame. When we ignite the gas as it issues directly from the glass tube, without using the platinum jet, the flame takes a yellow color from the sodium of the glass.

The hydrogen flame is intensely hot; in fact, its combustion indicates a higher temperature than an equal bulk of any other known substance. The great affinity of hydrogen for oxygen may be further illustrated by making a mixture of two volumes of the former to one volume of the latter, and applying flame, when a violent explosion will occur. The same takes place when air, in larger proportion, is used instead of oxygen; hence the importance of having all the air driven out of a generator before attempting to ignite the gas. Its affinity for most other substances is not sufficient to support their combustion when they are introduced in a burning condition into the gas. This may be illustrated by the following experiment, Fig. 40: If a cylinder of the gas is held in an inverted position, and a lighted taper or candle brought to the mouth, the gas will ignite, but on pushing the burning candle up through the flame into the pure gas, the combustion of the taper ceases, on account of the lack of affinity between its constituents and the hydrogen surrounding it. With chlorine or the other halogens hydrogen combines even more readily than with oxygen, but with most other non-metals it does not unite directly unless in the nascent state.

FIG. 40.



Hydrogen a non-supporter of combustion.

It changes the composition of some metallic compounds by removing the non-metals with which the metals are combined, leaving the latter in the free state; for example, when we pass the gas over metallic chlorides, sulphides, or oxides at a red heat, the combinations are destroyed, and new compounds of hydrogen with chlorine, sulphur, or oxygen are formed.

Uses.—Hydrogen has comparatively few uses in the free state. At one time, on account of its lightness, it was used for filling balloons. As a frequent constituent of natural gas and water-gas, it is useful on account of its great heating power. In the nascent state it is a valuable laboratory agent in the preparation of many chemical compounds.

PRACTICAL EXERCISES.

(1) Make hydrogen from zinc and sulphuric acid, using apparatus as arranged in Fig. 37, p. 126.

(2) Note its levity by collecting a tube full, and, holding it covered in a vertical position, bring a lighted taper a short distance above its mouth and remove the cover; the gas will rise to the flame and ignite.

(3) Another tube, similarly filled, is held in an inverted position and the cover removed; it will be found, even after the lapse of some time, that the hydrogen at the mouth of the tube may be ignited, thus demonstrating that the gas is too light to come down and out of the mouth of the tube.

(4) The two preceding experiments have demonstrated the combustibility of the gas, which, when pure, burns quietly, with a colorless flame. If, however, it be mixed with air and flame be applied, a violent explosion ensues. *Therefore the tube from the generator should never be brought near a flame until it is certain that all the air has been expelled;* this is determined by trying a test-tube full; if it burn quietly, the jet may be lighted. *This precaution should always be observed.*

(5) On bringing a lighted taper to the mouth of the inverted tube filled with hydrogen, the gas is ignited, but, on pushing the burning taper up into the gas, its flame is extinguished; thus showing that, while hydrogen is combustible, it is not a supporter of combustion.

(6) Continue the addition of acid to the zinc until the latter is nearly all dissolved; disconnect the apparatus, pour the liquid on a filter, collect the filtrate in a small beaker or evaporating dish, concentrate by heat, and set aside for twenty-four hours to crystallize. The crystals obtained are *zinc sulphate*, $ZnSO_4$, the result of a combination of the sulphuric acid and the zinc, as follows:

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

CHAPTER III.

THE HALOGENS.

CHLORINE.

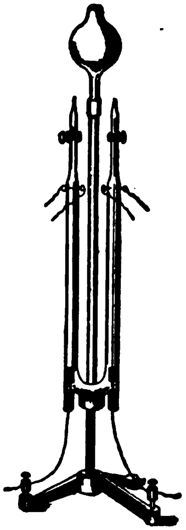
Symbol, Cl. *Atomic Weight*, 35.37. *Valence*, I.

History.—Chlorine was first prepared by Scheele, in 1774, while experimenting with "black magnesia" (an ore consisting largely of manganese dioxide) and hydrochloric acid, but its elementary character was first established by Davy, in 1801, who gave to it the name of chlorine on account of its greenish-yellow color.

Occurrence.—Chlorine does not occur in the free state in nature, but is found abundantly in combination with sodium, in sea water, and in the salt-wells of the United States; also as rock-salt in the mines of Austria, Spain, and Bavaria, all of which have been worked for centuries. It is also found in certain "horn" minerals, combined with lead, silver, or mercury.

In the vegetable kingdom chlorine is not very abundant, but in the animal kingdom, combined with sodium, it is found more abundantly, being a constituent of most animal secretions.

FIG. 41.



Decomposition of hydrochloric acid by electrolysis.

Preparation.—Chlorine may be prepared by a number of different processes, as follows:

(1) By the electrolysis of hydrochloric acid or of chlorides. The decomposition of the former is readily carried out in an apparatus shown in Fig. 41.

(2) By the decomposition of certain chlorides by heat, those of gold, palladium, and platinum giving up the gas most readily.

$$\underset{\text{Platinic Chloride.}}{PtCl_4} = \underset{\text{Platinous Chloride.}}{PtCl_2} + \underset{\text{Chlorine.}}{Cl_2}.$$

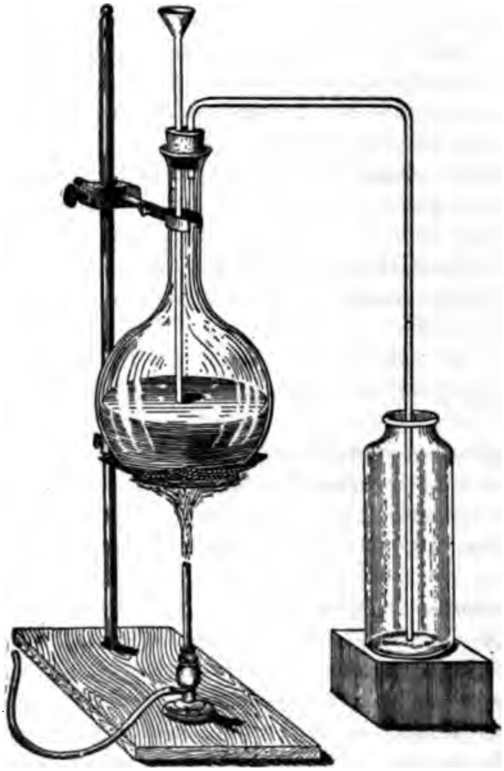
(3) On heating a mixture of manganese dioxide and hydrochloric acid, chlorine is given off abundantly, and may be col

lected over warm water, or by "downward displacement," as illustrated in Fig. 42. The reaction which takes place may be expressed as follows:

$$\underset{\substack{\text{Manganese}\\\text{Dioxide.}}}{MnO_2} + \underset{\substack{\text{Hydrochloric}\\\text{Acid.}}}{4HCl} = \underset{\substack{\text{Manganous}\\\text{Chloride.}}}{MnCl_2} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Chlorine.}}{Cl_2}.$$

This is the method of the U. S. Pharmacopœia. Care should be taken to mix the acid thoroughly with the powder, to prevent any of the latter from remaining unmoistened on the bottom and causing fracture of the flask on the application of heat. The oxide should be in excess of the acid, and heat should not be applied for some minutes after they are mixed, or the resulting gas will be mixed with hydrochloric acid. As an additional pre-

FIG. 42.



Preparation of chlorine.

caution it has been recommended to use the oxide in lumps, and have them above the surface of the acid; even then the gas should be passed through a small quantity of water, to remove the last traces of acid, before collecting it in the receiver.

(4) By mixing in an apparatus similar to that used in the preceding process, five parts of manganese dioxide, four parts of sodium chloride, and a mixture of twelve parts of sulphuric acid with six parts of water:

MnO_2	+	$2NaCl$	+	$2H_2SO_4$	=	$MnSO_4$	+	Na_2SO_4	+	$2H_2O$	+	Cl_2.
Manganese Dioxide.		Sodium Chloride.		Sulphuric Acid.		Manganous Sulphate.		Sodium Sulphate.		Water.		Chlorine.

This process has been recommended on the score of economy; but in these days of cheap hydrochloric acid this cannot be urged as a perceptible advantage over the preceding.

(5) Most peroxides and other oxidizing agents cause an evolution of chlorine when heated with hydrochloric acid, provided the corresponding chloride does not exist or is unstable. With potassium dichromate the reaction is as follows:

$K_2Cr_2O_7$	+	$14HCl$	=	Cr_2Cl_6	+	$2KCl$	+	$7H_2O$	+	$3Cl_2$.
Potassium Dichromate.		Hydrochloric Acid.		Chromic Chloride.		Potassium Chloride.		Water.		Chlorine.

(6) As a rapid method in the laboratory, hydrochloric or sulphuric acid added to bleaching powder will give an abundance of the gas:

$Ca(ClO)_2.CaCl_2$	+	$4HCl$	=	$2CaCl_2$	+	$2H_2O$	+	$2Cl_2$.
Bleaching Powder.		Hydrochloric Acid.		Calcium Chloride.		Water.		Chlorine.

This process is extensively used in bleaching and disinfecting operations.

(7) The process of Deacon, in which the hydrochloric acid from the Leblanc soda process is passed, with air, over pieces of brick saturated with cupric and sodium sulphates, and heated to about 500° to 700°, has been used largely in England for the preparation of chlorine to be used in the manufacture of bleaching powder. The exact chemical action of the salts of sodium and copper is not well understood, except that they enable the following reaction between the hydrochloric acid and the oxygen of the air to take place at a lower temperature than would the bricks alone:

$$4HCl \quad + \quad O_2 \quad = \quad 2H_2O \quad + \quad 2Cl_2.$$

This chlorine is mixed with some undecomposed hydrochloric acid and the nitrogen of the air, but is, nevertheless, adapted to the purposes for which it is used. Cuprous chloride has been employed in the place of cupric sulphate with somewhat better results; in fact, it has been shown that a number of substances bring about the action, notably magnesium oxide.*

(8) The method of Weldon has been used for the same purpose. This, however, is a modification of the decomposition of hydrochloric acid by manganese dioxide, adapted to an industrial scale, by which the latter compound is recovered and used for decomposing fresh quantities of hydrochloric acid indefinitely. More recently the Weldon-Pechiny process has been developed, and put in practical operation at Salindres, France, and near Birmingham, England.

This process consists in decomposing magnesium oxychloride by passing air over it at a temperature of 1000°. The magnesium salt is converted into oxide, while the chlorine, mixed with nitrogen and small quantities of hydrochloric acid, is passed through a purifying system, and then over lime, which it converts into bleaching powder. The magnesium oxychloride is prepared by dissolving magnesium oxide in the hydrochloric acid of the Leblanc process, or from the ammonium chloride of the ammonia-soda process. In both cases it utilizes what would otherwise be a waste product, it being possible to use the same magnesia indefinitely. The reaction which takes place may be considered a decomposition of magnesium chloride, since the oxychloride is made by mixing the oxide with the chloride:

$$\underset{\substack{\text{Magnesium}\\\text{Chloride.}}}{2MgCl_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\substack{\text{Magnesium}\\\text{Oxide.}}}{2MgO} + \underset{\text{Chlorine.}}{2Cl_2.}$$

It is claimed for the Weldon-Pechiny process that 72 per cent. of the hydrochloric acid can be recovered as chlorine, and more recently, by combination of this with the potassium chlorate process of Muspratt and Eschellmann, it is possible to recover 90 per cent. of the acid employed. As an objection to this and the preceding process, it is urged that the chlorine is diluted with nitrogen and air, to such an extent that it cannot be used in the preparation of bleaching powder. This is, however, contrary to the claims of the inventors.

(9) A more recent process is that of DeWilde and Reychler.

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*Journal of the Society of Chemical Industry, 1889, p. 286.

This consists in fusing together equivalent weights of crystalline magnesium sulphate ($MgSO_4.7H_2O$), magnesium chloride ($MgCl_2.6H_2O$), and manganous chloride ($MnCl_2.4H_2O$). They first liquefy in their water of crystallization, and then give off hydrochloric acid gas, leaving a pink, hygroscopic mass, consisting of magnesium sulphate, manganous chloride, and magnesium oxychloride. The anhydrous mixture is then heated to dull redness, when it evolves a further quantity of hydrochloric acid and some chlorine, and leaves a black, porous residue containing magnesium sulphate, and a substance called magnesium manganite, having the composition $Mg_3Mn_3O_8$. The porous lumps formed in this way are placed in an earthenware tube, surrounded by sheet iron, and the whole heated to about 450°. This tube is connected with two iron tubes, through one of which hydrochloric acid passes, and through the other a current of air. The farther end of the cylinder has a tube attached, which carries off the chlorine produced in the cylinder by the joint action of the hydrochloric acid and the air passing over the heated magnesium manganite. The following reactions are involved in the process :

$$(1)\quad \underset{\substack{\text{Magnesium}\\\text{Manganite.}}}{Mg_3Mn_3O_8} + \underset{\substack{\text{Hydrochloric}\\\text{Acid.}}}{16HCl} = \underset{\substack{\text{Manganous}\\\text{Chloride.}}}{3MnCl_2} + \underset{\substack{\text{Magnesium}\\\text{Chloride.}}}{3MgCl_2} + \underset{\text{Chlorine.}}{2Cl_2} + \underset{\text{Water.}}{8H_2O.}$$

$$(2)\quad \underset{\substack{\text{Manganous}\\\text{Chloride.}}}{3MnCl_2} + \underset{\substack{\text{Magnesium}\\\text{Chloride.}}}{3MgCl_2} + \underset{\text{Oxygen.}}{4O_2} = \underset{\substack{\text{Magnesium}\\\text{Manganite.}}}{Mg_3Mn_3O_8} + \underset{\text{Chlorine.}}{6Cl_2.}$$

The part played in the reaction by the magnesium sulphate appears to be that of preventing the fusion of the mass, and thus maintaining its porous nature. It is said that over 80 per cent. of the hydrochloric acid employed is converted into chlorine, and that four-fifths of the remainder are recovered.

For a number of years the decomposition of sodium chloride by electrolysis with production of chlorine and sodium hydrate has claimed the attention of chemists, since if this can be accomplished economically, two useful substances are obtained, without by-products. Although there have been many attempts and failures to work this process economically, there is now a possibility of it being perfected so as to make it the cheapest of all the methods hitherto proposed.

The industrial processes here given will be more fully explained under sodium carbonate ; but it may be remarked that as hydrochloric acid is a by-product in one of the world's greatest chemical industries, and magnesium chloride is at present allowed to run to waste, the process which utilizes them will be given the preference, and we will then find that for smaller operations bleaching powder is our cheapest source of chlorine.

Physical Properties.—Chlorine is a yellowish-green gas, of a suffocating odor and an astringent taste. At 200° it is 2.45 times heavier than air, which is exactly in accordance with the calculation based on its atomic weight, but at ordinary temperatures it is found to be 2.47. Under a pressure of six atmospheres at 0°, or at −40° under ordinary pressure, it is converted into a yellow liquid which has a specific gravity of 1.33, boils at −35.5°, and solidifies at −102°. Water at 10° is the best for dissolving chlorine, as at that temperature one volume takes up 2.58 volumes of the gas; below that temperature a crystalline compound, $Cl_2.10H_2O$, commences to separate out. These crystals may be dried between filter paper, and preserved in a sealed tube, where they do not decompose until a temperature of 38° is reached. If, however, they be exposed to the air, decomposition soon commences.

Chemical Properties.—Chlorine combines readily with hydrogen on the application of flame, or when exposed to the direct rays of the sun, forming hydrochloric acid. For oxygen it has very slight affinity, as it will not burn in air, or support ordinary combustion, unless it be that of a substance rich in hydrogen, like the wax or paraffin of a taper. This affinity for hydrogen is illustrated in its behavior toward a number of compounds. If a piece of filter paper be moistened with warm turpentine oil and plunged into a jar of chlorine, the oil bursts into flame, at the same time there is a copious evolution of black smoke from the liberated carbon. Marsh gas, CH_4, or olefiant gas, C_2H_4, mixed with chlorine, will burn on the application of flame, with abundant deposition of carbon. Phosphorus, antimony, copper, and a few other metals inflame when finely divided and poured into a jar of chlorine. On account of its affinity for hydrogen, chlorine is a powerful oxidizer, and for this reason is largely used as a bleaching and disinfecting agent. The reaction which takes place when chlorine bleaches organic matter in the presence of moisture, is first its combination with hydrogen, which liberates oxygen, and second the combination of this oxygen, in the nascent state, with the elements of the coloring matter, forming colorless compounds. When used for disinfecting, the compound known as *bleaching powder* or *chlorinated lime* is usually employed, either alone or mixed with diluted hydrochloric acid or vinegar.

Moisture is necessary in order to obtain good results in either bleaching or disinfecting, since perfectly dry chlorine does not bleach. It is also well to remember that only the organic colors are affected by chlorine; for this reason printing ink is not destroyed, on account of its containing lamp-black or carbon, while written characters are at once decolorized. Under the name of **aqua chlori**, U.S.P., the solution of the gas is official. The U.S. Pharmacopœia requires that the solution contain "at least 0.4 per cent. of the gas." Chlorine water is a transparent greenish-yellow liquid, with a specific gravity of 1.003. It should be preserved in well-stoppered bottles, protected from the light, as it decomposes into hydrochloric acid and oxygen according to the following reaction:

$$2Cl_2 + 2H_2O = 4HCl + O_2.$$

In addition to its use in medicine as a stimulant and antiseptic, chlorine water is a valuable laboratory reagent, being especially employed for liberating iodine and bromine from combination, and for oxidizing many metallic compounds.

PRACTICAL EXERCISES.

(1) Make chlorine from manganese dioxide and hydrochloric acid, as shown in Fig. 42, p. 132.

(2) Pass the gas into water; it is absorbed; if this be continued until the water is saturated, it will be found to have absorbed about twice its volume of the gas; the chlorine water, **aqua chlori**, of the Pharmacopœia is the resulting product.

(3) A tube full of the gas, held with mouth upward and a lighted taper applied, fails to ignite, indicating that the gas is not combustible. Push the lighted taper into the gas; it is extinguished, or only burns with a small, dense, smoky flame, the result of a combination of the chlorine with the hydrogen of the material composing the taper, whereby carbon is liberated.

(4) Into a tube full of the gas put a piece of brightly dyed calico or blue litmus paper, previously moistened; it is rapidly bleached. Written characters on paper are similarly decolorized, but printed characters are not affected, as the latter contain carbon, in the form of lamp-black, which is not acted on by the gas.

HYDROGEN AND CHLORINE.

HYDROCHLORIC ACID.

Formula, HCl. *Molecular Weight*, 36.37.

History.—Hydrochloric acid in solution was known to the ancients, the alchemists being familiar with *aqua regia*, obtained by distilling nitre, sal ammoniac, and vitriol together. Glauber, about the year 1648, first prepared the aqueous acid, and gave it the name of *spiritus salis*, which as "spirits of salt" it retains to the present day. Priestley first collected the gas by the use of a pneumatic trough containing mercury. Davy, in 1810, disproved its supposed elementary character, and demonstrated it to be a compound of chlorine and hydrogen.

Occurrence.—Hydrochloric acid occurs uncombined in the gases from certain volcanoes, and in the rivers of South America which originate in the volcanic regions of the Andes.

Preparation.—When equal volumes of chlorine and hydrogen are mixed and exposed to diffused daylight, they slowly combine, forming hydrochloric acid, which may easily be shown to possess properties entirely different from either of its constituents. This combination may be effected at once and with explosion by exposing the mixture to the direct rays of the sun, to the light of the electric arc, to burning magnesium, or by the application of flame. For laboratory purposes the gas may be prepared in a flask with suitable attachments for washing and purifying, as in Fig. 43, by adding to sodium chloride one and a half times its weight of sulphuric acid, previously diluted with half its weight of water, and applying heat. A small quantity of sulphuric acid is put in the wash bottle to remove moisture, and the gas is then collected over mercury. When two molecules of sodium chloride (116.74 parts) and one molecule of th acid (97.82 parts) are taken the following reaction occurs:

$$\underset{\substack{\text{Sodium}\\\text{Chloride.}}}{2NaCl} + \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{H_2SO_4} = \underset{\substack{\text{Sodium}\\\text{Sulphate.}}}{Na_2SO_4} + \underset{\substack{\text{Hydrochloric}\\\text{Acid.}}}{2HCl.}$$

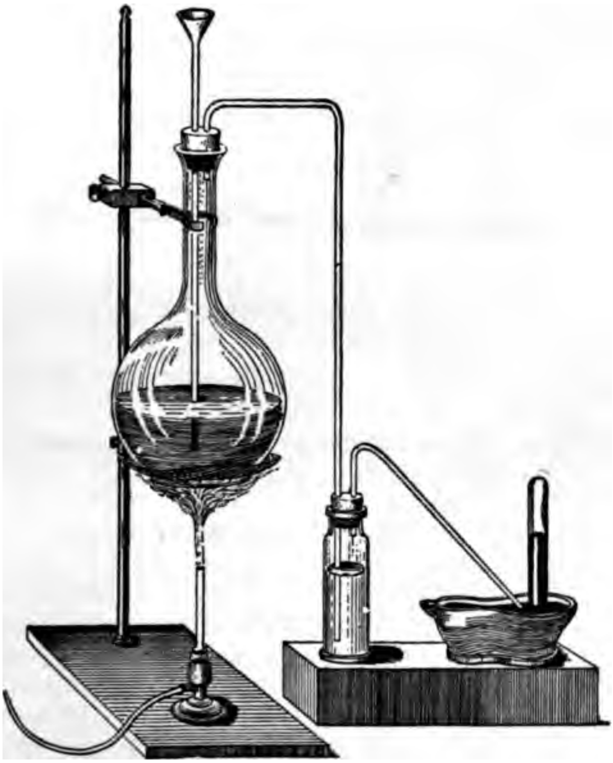
In working on a small scale, however, it is better to use th proportion of one molecule of each, when a more soluble ac sodium sulphate remains in the flask:

$$\underset{\substack{\text{Sodium}\\\text{Chloride.}}}{NaCl} + \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{H_2SO_4} = \underset{\substack{\text{Acid Sodium}\\\text{Sulphate.}}}{NaHSO_4} + \underset{\substack{\text{Hydrochloric}\\\text{Acid.}}}{HCl.}$$

This reaction occurs with the aid of less heat than is requir in the first, and is in other ways more satisfactory.

Properties.—Hydrochloric acid is a colorless gas, of a shar suffocating odor and an acid taste. It has a specific gravit compared with air, of 1.278, and may therefore be collected li chlorine by downward displacement. It has been liquefied by pressure of forty atmospheres and a temperature of 10°, or two atmospheres at —70°. In the liquid state it has a specific gravity of 0.908 at 0°, and boils at —35°. As a liquid it has but feeble solvent action on most substances, aluminum alone, among the metals, being attacked by it. The gas is very soluble in water; at 0° one volume of water will absorb about 503 volumes of the gas. It is neither combustible nor a supporter of combustion unless it be of metallic sodium, potassium, or magnesium, in which case hydrogen is evolved and a chloride of the metal formed. Certain oxides may be decomposed by the gas, with the formation of water and a chloride.

FIG. 43.



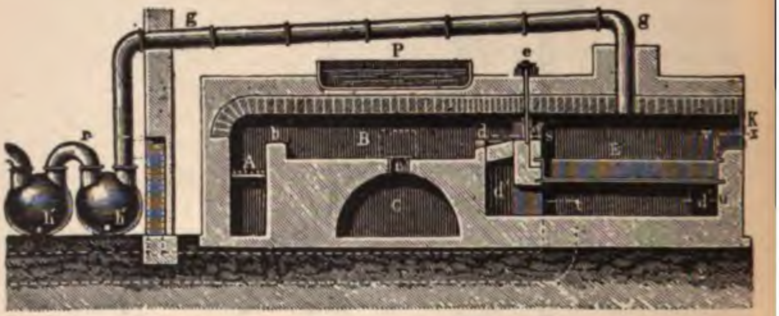
Preparation of hydrochloric acid.

Acidum Hydrochloricum, U.S.P.—This and the muriatic or hydrochloric acid of commerce are aqueous solutions of the gas in water. The official acid has a specific gravity of 1.163, and contains 31.9 per cent. of the gas. The commercial acid is a by-product in the Leblanc soda process, in which the gas is produced from salt and sulphuric acid, according to the reactions above given, but the method of dissolving the gas is different.

The decomposition of the salt is carried out in what is known as a salt-cake furnace, as shown in Fig. 44. It consists of two important parts,—namely, the pan, E, in which the sulphuric acid and salt are mixed and heated, and the muffle, B, in which the mixture is further heated at a higher temperature in order to complete the decomposition and drive off the remainder of the hydrochloric acid gas.

This gas is then forced through the pipe, *g g*, into the stoneware vessels, *h′ h′*, or else through a system of tall towers in which are coke or bricks, and over these a constant stream of water trickles, carrying down with it the absorbed gas, until, when the bottom is reached, a strong, nearly saturated solution is the result.

FIG. 44.



Commercial preparation of hydrochloric acid.

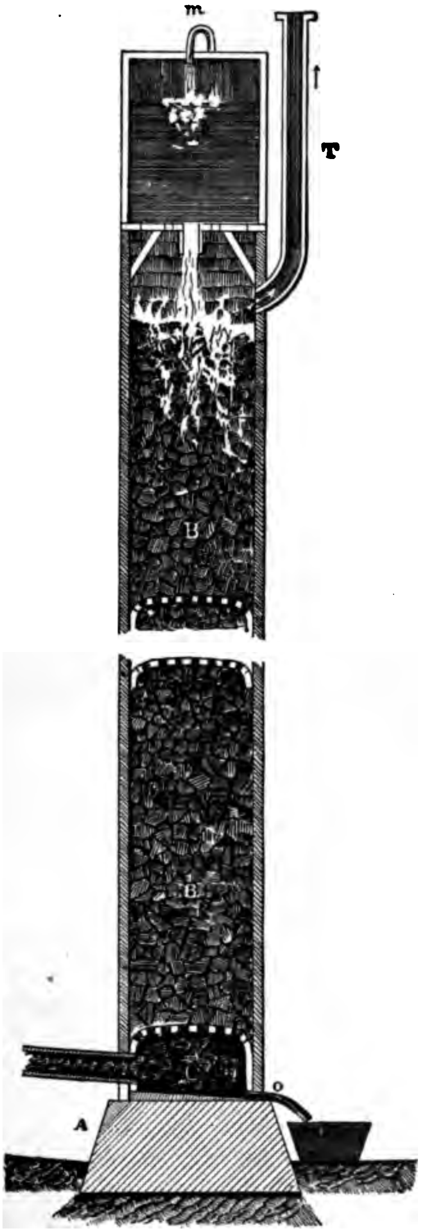
This solution is then run off into suitable receivers. Such a tower is shown in Fig. 45. There are rarely less than two of them associated with each salt-cake furnace, and the gas which escapes condensation in the first one is conveyed to the bottom of the second and forced up through it.

The acid thus prepared is of a pale-yellow color, due to small quantities of ferric chloride, organic matter, and other impurities difficult to remove. When the pure acid is desired it is necessary to make it in glass vessels from pure materials. The pure acid is colorless, of a pungent odor, and a very sour taste. It fumes strongly when exposed to the air, and gives off hydrochloric acid gas when heated, until the solution is reduced to a strength, under ordinary pressure, of 20.24 per cent., when it distils unchanged at 110°. When a weak acid is heated, water distils over until the solution reaches the strength of 20.24 per cent., when it distils unchanged.

Hydrochloric acid possesses the chemical properties of an energetic acid. It decomposes carbonates, phosphates, and most other salts, and dissolves nearly all the metals. Its action is without the oxidizing effect which usually accompanies nitric acid.

Impurities.—Hydrochloric acid is not often adulterated, but may contain impurities acquired in its manufacture or from carelessness in handling. It should leave no residue on evaporation to dryness, showing the absence of saline impurities and organic matter. On diluting with four volumes of water, and saturating with hydrogen sulphide, no precipitate or coloring should occur, indicating freedom from lead, arsenic, tin, thallium, and copper; nor should it acquire a blue color with ammonia in excess (cop-

FIG. 45.



Coke tower.

per). Potassium sulphocyanate should not cause a red color (iron). A cold, dilute solution of starch and potassium iodide should not give a blue color (chlorine). When the acid is diluted with two volumes of water and placed in a test-tube with a small piece of zinc, no color should be imparted to a loose plug of cotton moistened with lead acetate solution and placed in the upper part of the tube (sulphurous acid); nor to a piece of filter paper moistened with one drop of silver nitrate solution and placed above the cotton (arsenic). When diluted with ten volumes of water, no precipitate should occur on the addition of a few drops of barium chloride solution (sulphates). Ten volumes of the acid mixed with twenty volumes of water and agitated with one volume of chloroform should impart to the latter no color (iodine and bromine). The presence of free chlorine may indicate that nitric or nitrous acid is present. This may be definitely determined by adding a piece of gold leaf, warming for some minutes, and then testing the solution with stannous chloride for gold, or by adding sodium hydrate to the original acid until strongly alkaline, and heating with pure zinc, when, if nitric or nitrous acid be present, ammonia will be evolved, and may be detected by holding a piece of moistened red litmus paper in the mouth of the tube.

Chlorides.—The compounds of hydrochloric acid are known as chlorides, and they are usually formed by dissolving the metal, a hydrate, or carbonate in the acid. A few are made by the direct action of chlorine on the metal. Nearly all metallic chlorides are soluble in water, the exceptions being the chlorides of silver, mercury (ous), and lead, the last of which is soluble in hot water.

Tests.—Hydrochloric acid and chlorides are detected by the insoluble white precipitates formed with silver, mercurous, or lead nitrates. The first forms silver chloride, $AgCl$, soluble in ammonium hydrate, the second mercurous chloride, Hg_2Cl_2 (calomel), which blackens on the addition of ammonium hydrate, and the third lead chloride, $PbCl_2$, which is soluble in hot water.

Uses.—Both hydrochloric acid and the chlorides are extensively used in medicine and the arts. There is scarcely an industry in which hydrochloric acid is not largely consumed. The greatest production of it is as a by-product in the soda industry, from which it goes to be converted into chlorine to furnish bleaching powder.

PRACTICAL EXERCISES.

(1) Make hydrochloric acid by taking one test-tube full of hydrogen and another of chlorine, bring their mouths together (the hydrogen tube above with mouth down, as it is lighter), turn over once or twice, so as to thoroughly mix, and open their mouths to a flame; a sharp report will occur, with the development of strongly acid fumes, which may be recognized by silver nitrate as *hydrochloric acid.*

(2) Prepare a quantity of hydrochloric acid gas, using the same or similar apparatus to that employed in the preparation of chlorine. Place some sodium chloride (common salt) in the flask and slowly add sulphuric acid; when the evolution of gas ceases, apply a gentle heat. The gas, being heavier than air, may be collected by placing the delivery-tube in a jar or test-tube. When it is desired to have the gas pure, it should be dried by passing through sulphuric acid, and then collecting over mercury.

(3) Fill a dry test-tube, or jar, with the gas, cover, and, having inverted the vessel and brought its mouth under water, remove the cover; the water so readily absorbs the gas that it rises and nearly fills the vessel. More of the solution may be made by passing the gas into water. The resulting solution, when of proper strength, is the **acidum hydrochloricum** of the Pharmacopœia.

(4) A piece of moistened blue litmus paper is instantly reddened when held in a tube of the gas, indicating its acid nature.

(5) A lighted taper applied to the gas fails to ignite it, and is extinguished if lowered into it, thus showing that the gas is neither combustible nor a supporter of combustion.

(6) Bring a rod moistened with ammonia water over the mouth of a tube full of the gas; dense white fumes of ammonium chloride are formed.

(7) Dissolve the mixture remaining in the flask, after the hydrochloric acid gas has been prepared, in warm water, add sodium carbonate so long as active effervescence ensues, whereby the excess of sulphuric acid is neutralized. The solution, when filtered, concentrated, and set aside, yields crystals of *sodium sulphate* (Glauber salt).

BROMINE.

Symbol, Br. *Atomic Weight,* 79.76. *Valence,* I.

History.—This element was discovered in 1826 by Balard, of Montpellier, France, in the bittern from the manufacture of salt on the Mediterranean.

Occurrence.—Bromine occurs chiefly as magnesium bromide in sea water, and as the magnesium, calcium, or sodium salt in many rock-salt deposits and salt-wells. Large quantities of bromine are produced at Stassfurt, a considerable quantity is manufactured from the residues after the preparation of iodine from kelp, but the greatest portion of the world's supply comes from the salt-wells of the United States.

The first production of bromine in this country was at Freeport, in Pennsylvania, in 1846; but it was not until 1866, when bromides came into use in medicine, that the industry assumed significant proportions. In 1871 shipments commenced to Europe, and in 1891 the production amounted to 415,000 pounds, divided as follows: Pennsylvania, 140,000 pounds; West Virginia, 120,000 pounds; Ohio, 110,000 pounds; and Michigan, 45,000 pounds. The production for 1892 and 1893 was 379,480 pounds and 348,399 pounds respectively.

Bromine has also been found in certain cruciferous plants, and in many marine plants and animals, but it does not naturally occur anywhere in the free state.

Preparation.—The bittern, which is the mother liquor from the crystallization of salt, is concentrated to about 45° B., which causes the separation of the more insoluble sulphates and chlorides, and then manganese dioxide and sulphuric acid are added, which liberate the bromine, according to the following reaction:

$$\underset{\substack{\text{Magnesium}\\ \text{Bromide.}}}{MgBr_2} + \underset{\substack{\text{Manganese}\\ \text{Dioxide.}}}{MnO_2} + \underset{\substack{\text{Sulphuric}\\ \text{Acid.}}}{2H_2SO_4} = \underset{\substack{\text{Magnesium}\\ \text{Sulphate.}}}{MgSO_4} + \underset{\substack{\text{Manganous}\\ \text{Sulphate.}}}{MnSO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\substack{\text{Bro-}\\ \text{mine.}}}{Br_2}.$$

The application of heat completes the reaction. The vapors are conducted through a condensing apparatus into well-cooled receivers. The bromine is afterward purified from water by distillation over calcium chloride, and from chlorine by distilling with a bromide, which liberates bromine and forms a chloride:

$$\underset{\substack{\text{Potassium}\\ \text{Bromide.}}}{2KBr} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\substack{\text{Potassium}\\ \text{Chloride.}}}{2KCl} + \underset{\text{Bromine.}}{Br_2}.$$

Another method, used on a large scale at Stassfurt, is the continuous process of decomposing the bromides by a current of chlorine and steam. The liquor flows into the top vessel of a series, arranged in a terrace, while the chlorine passes into the lowest vessel, meeting the nearly-exhausted bromide liquor. The bromine passes out of the highest vessel and is condensed by suitable means.

Properties.—Bromine is a dark, reddish-brown, volatile liquid, of a suffocating odor and a caustic taste. When exposed to the air orange-red vapors are constantly evolved, which strongly attack the eyes. The name, from βρωμος, stench, was given it on account of its disagreeable odor. Its specific gravity at 15° is 2.99. Pure bromine boils at 58.7°, and when cooled solidifies to brown-gray, crystalline scales, like iodine, which melt at —7.05°.

Bromine is soluble in thirty parts of water at 15°, and readily soluble in alcohol, ether, chloroform, and carbon disulphide, the last three being capable of extracting it from its aqueous solution on agitation. It is also soluble in solution of potassium or sodium bromide and in hydrobromic acid. The saturated solution in water is of a reddish-brown color, and contains at 15° one part bromine in twenty-nine parts of water. At —2° a crystalline hydrate, $Br_2.10H_2O$, separates, which decomposes at 6.2°.

In chemical properties bromine closely resembles chlorine, although it usually acts with less energy. It is not combustible, nor will it support ordinary combustion, unless it be that of a jet of burning hydrogen lowered into its vapor. With many metals it combines directly, forming bromides, a notable example being potassium, with which it combines with explosive violence; but with sodium the union is extremely slow, it being possible to boil the two together without causing perceptible action. Bromine possesses the property of bleaching organic compounds, but in a less degree than chlorine. It bleaches litmus and indigo solutions and colors solution of starch yellow.

Impurities and Tests.—Bromine should vaporize completely without residue. If three grammes of bromine be mixed with 30 c.c. of water, and enough ammonia water added to render the solution colorless, the liquid then digested with barium carbonate, filtered, evaporated to dryness, and the residue gently ignited, the latter should be soluble in absolute alcohol without leaving more than 0.26 gramme of residue, indicating the absence of more than 3 per cent. of chlorine. This test is founded on the fact that barium bromide is soluble and barium chloride insoluble in absolute alcohol.

If an aqueous solution of bromine be poured upon reduced iron, and shaken with the latter until nearly colorless, then filtered, mixed with gelatinized starch, and a few drops of bromine water be carefully poured on top, not more than a very faint blue zone should appear at the line of contact of the two liquids; such a blue zone would indicate iodine.

Uses.—In the free state bromine is used in the manufacture of bromides and of many bromine derivatives of the coal-tar compounds. It has also been used in medicine, internally, when largely diluted, as an alterative, like iodine, and externally as a caustic and for dissolving gangrene. It is also extensively used as a disinfectant. At Johnstown, Pennsylvania, in 1889, over six thousand pounds were used for disinfecting purposes.

PRACTICAL EXERCISES.

(1) Pass chlorine into a dilute (about 1 per cent.) solution of potassium bromide; the liquid will become reddish-brown in color, owing to separation of bromine, which remains dissolved in the water.

(2) To a portion of the liquid resulting from the above experiment add a solution of starch; a yellow color will be developed, due to the formation of a compound of starch with bromine.

(3) To the remainder of the solution in a test-tube add a few drops of chloroform and agitate; the chloroform will remove the bromine from the water, and will settle to the bottom of the tube as a deep, reddish-brown liquid, while the water above will become nearly colorless.

BROMINE AND HYDROGEN.

HYDROGEN BROMIDE.

Formula, HBr. *Molecular Weight*, 80.76.

Preparation.—When equal volumes of hydrogen and bromine vapor are mixed, they do not explode by the application of flame as in the case of hydrogen and chlorine, but when the mixture is passed over red-hot platinized asbestos, combination takes place and hydrogen bromide or hydrobromic acid gas results. The same compound is formed when a jet of hydrogen is burned in bromine vapor. A more practical method is to take one part of amorphous phosphorus, mix it with two parts of water, in a flask to which is fitted, with a good cork, a stoppered funnel tube containing ten parts of bromine. The apparatus may be arranged as in Fig. 46.

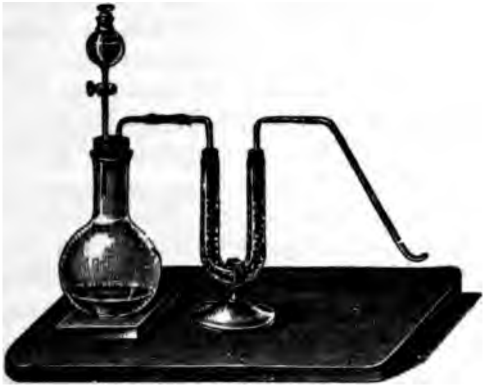
The stop-cock is opened so as to allow the bromine to run in drop by drop, when the following reactions take place:

$$\underset{\text{Phosphorus.}}{P_4} + \underset{\text{Bromine.}}{10Br_2} = \underset{\substack{\text{Phosphorus}\\ \text{Pentabromide.}}}{4PBr_5}.$$

$$\underset{\substack{\text{Phosphorus}\\ \text{Pentabromide.}}}{PBr_5} + \underset{\text{Water.}}{4H_2O} = \underset{\substack{\text{Hydrogen}\\ \text{Bromide.}}}{5HBr} + \underset{\substack{\text{Phosphoric}\\ \text{Acid.}}}{H_3PO_4}.$$

The action is somewhat violent at first, and great care shou be exercised during the operation to thoroughly agitate t mixture in order to bring the two elements in contact, and pr vent the collection in one place of any appreciable quantity bromine. The escape of any free bromine is prevented by co necting the flask with a tube containing amorphous phospho mixed with pieces of glass. By this means the hydrogen bromide formed in the flask is augmented by that formed in the tube. After the first action ceases it is necessary to apply a gentle heat, when the gas comes off freely, and is best collected by downward displacement. Hydrobromic acid attacks mercury somewhat, so it is not a suitable medium over which to collect it, as was the case with hydrochloric acid.

FIG. 46.



Preparation of hydrobromic acid.

By heating together potassium bromide and phosphoric acid the gas is evolved as follows:

$3KBr$	+	H_3PO_4	=	K_3PO_4	+	$3HBr$.
Potassium Bromide.		Phosphoric Acid.		Potassium Phosphate.		Hydrobromic Acid.

It naturally occurs to one that a cheaper acid, like sulphuric, might be substituted; this, however, cannot be done in the case of the gas, but only in the preparation of the aqueous solution, since in the concentrated solution a decomposition takes place as follows:

$2KBr$	+	$3H_2SO_4$	=	$2KHSO_4$	+	$2H_2O$	+	SO_2	+	Br_2.
Potassium Bromide.		Sulphuric Acid.		Acid Potassium Sulphate.		Water.		Sulphur Dioxide.		Bromine.

Properties.—Hydrogen bromide is a colorless, heavy gas, with a sharp, irritating odor and an acid taste and reaction. At a temperature of —73° it becomes a colorless liquid, which, by a further reduction of temperature to —87°, forms an ice-like solid. The gas has a specific gravity of 2.8 (air = 1), and is very soluble in water. It is neither combustible nor a supporter of combustion. Chlorine readily decomposes hydrogen bromide according to the following reaction:

$$2HBr + Cl_2 = 2HCl + Br_2.$$

Many metals react with hydrogen bromide, forming bromides.

Acidum Hydrobromicum Dilutum, U. S. P.—As stated above, the gas is very soluble in water, and on account of its use in medicine this solution is worthy of especial consideration. Water saturated with the gas at 0° furnishes a solution which fumes strongly on exposure to the air, and has a specific gravity of 1.78. According to Biel, that of 50 per cent. strength has a specific gravity of 1.513 at 15°.

The official acid contains 10 per cent. of hydrobromic acid gas, and has a specific gravity, according to the Pharmacopœia, of about 1.077, which, as pointed out by Dr. Squibb, should be 1.0698. On the application of heat the strong acid gives off gas until the strength is reduced to 48 per cent., when it distils unchanged at a temperature between 125° and 126°, and possesses a specific gravity of 1.49 at 15°. When a weaker acid is heated, water distils over until the contents of the still reach the above strength, when it passes over unchanged. Like hydrochloric acid, the strength of the distillate varies according to the pressure.

An acid of 34 per cent. strength may be prepared by Dr. Squibb's method,* and then diluted to a 10 per cent. strength.

An acid of 48 per cent. strength may be prepared as follows: One hundred grammes of coarsely-powdered potassium bromide and 150 c.c. of sulphuric acid, specific gravity 1.41, are moderately warmed until solution is effected, and then distilled. Boiling commences at 126°, and the temperature slowly rises to 150°. During this time most of the hydrobromic acid distils over. Traces of sulphuric acid are carried over with the last portions of the distillate, and if the bromide contain bromate the first portions of the distillate will contain bromine.

A method frequently used when a dilute acid is desired consists in passing hydrogen sulphide into an aqueous solution of bromine containing some undissolved bromine. The reaction takes place as follows:

$$\underset{\text{Bromine.}}{Br_2} + \underset{\text{Hydrogen Sulphide.}}{H_2S} = \underset{\text{Hydrogen Bromide.}}{2HBr} + \underset{\text{Sulphur.}}{S.}$$

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* American Journal of Pharmacy, 1878, p. 116.

As fast as the bromine which is in solution is taken up more is dissolved, until enough hydrogen bromine is formed to act as a solvent of the bromine, and thus enable the process to continue rapidly. This method cannot be employed for any but dilute solutions. The excess of hydrogen sulphide is removed by evaporation, and the sulphur which separates is removed by filtration.

Fothergill's process is intended to furnish extemporaneously a solution of about 10 per cent. strength. It consists in taking 10 grammes of potassium bromide and 12 grammes of tartaric acid, each in 30 c.c. of distilled water, mixing, cooling, and, after standing one hour, pouring on a muslin strainer and washing with a little ice-cold water.

The impurities in diluted hydrobromic acid are usually accidental, and due to carelessness in manufacturing. Sulphuric acid, which might be present from this cause, is easily detected by solution of barium chloride. Hydrochloric acid is found by the partial or complete solubility, in ammonium hydrate, of the precipitate with silver nitrate. On evaporating the acid there should be no residue. This last test would detect the potassium bromide and bitartrate, which are found in the acid when made by Fothergill's formula.

Bromides.—The salts of hydrobromic acid and bromine are called bromides. Many of them can be prepared by the action of the acid on a carbonate, hydrate, or oxide; but they are oftener made from bromine, by first combining it with a metal like iron, and then decomposing by a carbonate or hydrate.

Potassium, sodium, lithium, and ammonium bromides are used medicinally, and silver bromide is used extensively in photography. Nearly all the bromides are soluble in water, the notable exceptions being those of silver, mercury, and lead. Heat fuses and volatilizes the bromides, most of them with decomposition, accompanied by liberation of bromine. They are all decomposed by chlorine, sulphuric and nitric acids.

Both the acid and its salts are detected by the addition of a dilute solution of starch and chlorine water, which form the yellow starch bromide. The bromine is easily soluble in, and separated by agitation with, ether, chloroform, and carbon disulphide; to all of these it imparts a reddish-brown color, the shade of color depending on the concentration.

BROMINE AND CHLORINE.

Bromine Monochloride.—When chlorine is passed into bromine at a low temperature, large quantities are absorbed, and a reddish-yellow volatile liquid, bromine monochloride, $BrCl$, is formed. It is soluble in water, and separates a hydrate on cooling to 0°. It is decomposed at or above 10°.

IODINE.

Symbol, I. *Atomic Weight*, 126.53. *Valence*, I.

History.—In 1811, Courtois, a soap-boiler of Paris, noticed a peculiar corrosion of his copper kettle during the evaporation of kelp liquor, after crystallizing the sodium carbonate from it; and subsequently he obtained violet vapors on the addition of sulphuric acid to some of the waste liquor.

This discovery was announced in 1812. Davy and Gay-Lussac both investigated the new element about a year later, and the latter gave it the name of iodine from the violet color of its vapor.

Occurrence.—Iodine does not occur in the free state in nature, but in combination with potassium, sodium, or magnesium; it is found in the waters of many mineral springs, in sea water, in most sea plants and animals, in rock-salt, and in coal. In certain minerals it occurs combined with silver, lead, mercury, and zinc. The sodium nitrate, or Chili saltpetre, of Peru and Chili, contains iodine in the form of sodium iodate.

Source.—The world's supply of iodine comes from two sources, sea plants and Chili saltpetre. The former of these has been worked since the first demand for the element. The relative quantity occurring in sea water is too minute for that to be considered a source, but certain sea plants absorb the iodides in considerable quantity. Of these the *Algæ* have the greatest absorbing power, and two or three species of *Laminaria* are said to furnish the only weeds now used in this industry.

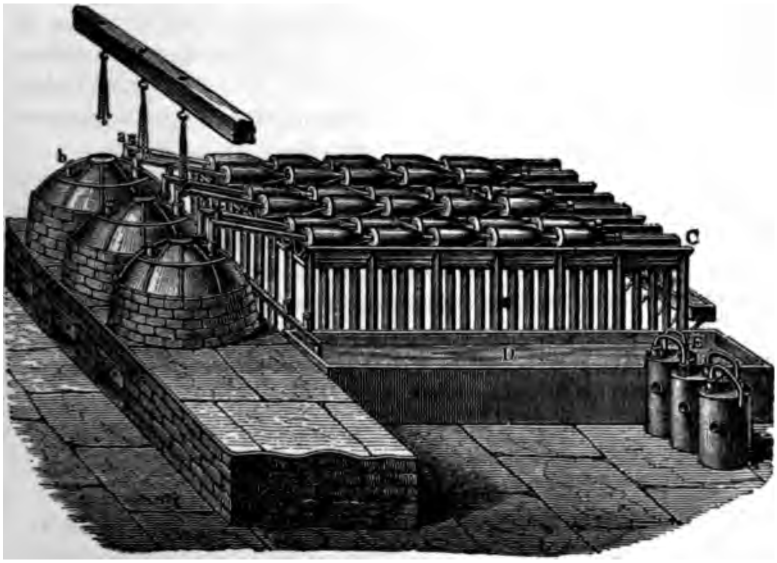
Preparation.—The sea-weeds which collect on the coasts of Scotland, Ireland, and some of the neighboring islands are gathered, and, with those brought in vessels sent out for the purpose, are burned, the ash forming what has for a long time been known as *kelp*. The similar product from the coasts of Normandy and the Channel Islands is called *varec*, and that from the Spanish coasts is known as *barilla*. These three commercial products were long worked for their sodium carbonate, but at the present time they are worked for the iodine they contain. The method of manufacture may be briefly outlined as follows:

Sea-weeds are burned to a fused mass of carbon and ash ; this mass is lixiviated with water, the solution evaporated to remove chlorides, sulphates, and carbonates, and the concentrated mother liquor treated with sulphuric acid, which causes a separation of sulphur on account of the sulphides and sulphites present. This sulphur and the crystals of sulphate formed are removed, and the remaining acid liquor, in a lead-lined retort, is treated with manganese dioxide, which, with the free sulphuric acid previously added, liberates iodine according to the following reaction :

$$\underset{\substack{\text{Potassium}\\\text{Iodide.}}}{2KI} + \underset{\substack{\text{Manganese}\\\text{Dioxide.}}}{MnO_2} + \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{2H_2SO_4} = \underset{\substack{\text{Potassium}\\\text{Sulphate.}}}{K_2SO_4} + \underset{\substack{\text{Manganous}\\\text{Sulphate.}}}{MnSO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Iodine.}}{I_2}.$$

The temperature is kept at about 60°, which causes the iodine to pass off in vapor and condense in a series of earthenware receivers adapted to the retort for that purpose. The apparatus by which the sublimation and condensation are accomplished is shown in Fig. 47. After iodine ceases to be evolved, bromine is liberated and conducted into separate receivers. The above method has been carried out at Glasgow, which has always been the seat of the iodine industry. Within the last few years, how-

FIG. 47.



Sublimation of iodine.

ever, competition with the cheaper sources in Peru and Chili has led to improvements in the manner of heating the sea-weed, so as to reduce the loss by decomposition and volatilization, and at the same time the by-products are saved and utilized. In one of these, the "char" process, the sea-weed is heated in iron retorts at a low temperature. Acetic acid, tar, and ammonia distil over, all of which can be utilized, while in the retort there remains a large quantity of charcoal, which, after treatment with water to remove iodides and other salts, can be used. Another, the "wet" process, consists of a still more radical change. The air-dried sea-weed is boiled with a solution of sodium carbonate and filtered; the precipitate or insoluble portion remaining on the filter is composed largely of cellulose. The filtrate is acidified with sulphuric acid, by which algin is precipitated. The solution, after removal of algin, is neutralized with calcium carbonate, evaporated, the easily crystallized salts removed, and the mother liquor treated for iodine in the usual manner. This process, in addition to increasing the yield of iodine, reduces the cost materially by the value of the algin and cellulose, both of which are useful in many ways.

In France chlorine is employed to separate the iodine from the liquor, instead of sulphuric acid and manganese dioxide, as follows:

$$\underset{\substack{\text{Potassium}\\\text{Iodide.}}}{2KI} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\substack{\text{Potassium}\\\text{Chloride.}}}{2KCl} + \underset{\text{Iodine.}}{I_2}$$

The most important sources of iodine at the present time are the nitre beds of Chili and Peru. So great has become this industry in South America that the yearly output from that source amounted in 1891 to 949,805 pounds. The iodine exists in the mother liquor from the sodium nitrate in the form of sodium iodate, $NaIO_3$; from which it is precipitated by sodium bisulphite and sulphurous oxide, as follows:

$$\underset{\substack{\text{Sodium}\\\text{Iodate.}}}{2NaIO_3} + \underset{\substack{\text{Sodium}\\\text{Bisulphite.}}}{4NaHSO_3} + \underset{\substack{\text{Sulphur}\\\text{Dioxide.}}}{SO_2} = \underset{\substack{\text{Sodium}\\\text{Bisulphate.}}}{4NaHSO_4} + \underset{\substack{\text{Sodium}\\\text{Sulphate.}}}{Na_2SO_4} + \underset{\text{Iodine.}}{I_2}$$

The iodine is collected on muslin strainers, dried, and purified by sublimation.

According to another method, the sodium iodate is first reduced to iodide, as follows:

$$\underset{\substack{\text{Sodium}\\\text{Iodate.}}}{NaIO_3} + \underset{\substack{\text{Sodium}\\\text{Bisulphite.}}}{3NaHSO_3} = \underset{\substack{\text{Sodium}\\\text{Bisulphate.}}}{3NaHSO_4} + \underset{\substack{\text{Sodium}\\\text{Iodide.}}}{NaI}$$

This sodium iodide is then treated with copper sulphate and ferrous sulphate, which precipitate the iodine as cuprous iodide:

$$\underset{\substack{\text{Sodium}\\\text{Iodide.}}}{2NaI} + \underset{\substack{\text{Copper}\\\text{Sulphate.}}}{2CuSO_4} + \underset{\substack{\text{Ferrous}\\\text{Sulphate.}}}{2FeSO_4} = \underset{\substack{\text{Cuprous}\\\text{Iodide.}}}{Cu_2I_2} + \underset{\substack{\text{Sodium}\\\text{Sulphate.}}}{Na_2SO_4} + \underset{\substack{\text{Ferric}\\\text{Sulphate.}}}{Fe_2(SO_4)_3}.$$

The cuprous iodide is collected and heated with manganese dioxide and sulphuric acid, and the iodine sublimed therefrom in the usual manner.

Iodine for medicinal purposes is purified by washing with cold water, drying, and subliming. The first portions which come over are set aside, as possibly containing iodine cyanide, and the remainder sublimed at the temperature of a water bath.

Properties.—Iodine, U.S.P., consists of "heavy, bluish-black, dry and friable rhombic plates, of a metallic lustre, a distinctive odor, a sharp and acrid taste, and a neutral reaction." It has a specific gravity of 4.948 at 17°, melts at 114°, and boils at about 184°, giving off a vapor which, when mixed with air, is violet colored, but when pure is deep blue. At ordinary temperatures slow volatilization takes place, and, if in a bottle, minute crystals are deposited on the sides. Below 500° the vapor has a density of 127, which indicates that the molecule consists of two atoms, I_2, but above 500° the vapor density diminishes until 1500° is reached, when it has fallen to 65.7, or a little above the theory for I_1, which indicates that dissociation occurs at high temperatures.

Iodine is slightly soluble in water, one part of the element requiring 5524 parts of water at 10° to dissolve it, forming a peculiar yellowish solution, which, on exposure to light, forms hydriodic acid. The solubility of iodine in water is much increased by the presence of potassium iodide or hydriodic acid. The official **Liquor Iodii Compositus,** U.S.P. (Lugol's Solution), is a preparation based on this property. In strong alcohol iodine is soluble to the extent of one part to ten of the solvent, forming a dark-brown liquid, which is stronger than the **Tinctura** Iodi, U. S. P., which contains seven parts of iodine in one hundred of alcohol. Iodine is also soluble in ether, chloroform, carbon disulphide, benzene, and petroleum, to all of which, in small quantity, it imparts a red or violet color, according to the amount dissolved. It is also soluble in glycerin and in glacial acetic acid. The solubility is increased in water by a number of organic substances, notably tannic acid.

In chemical properties iodine resembles chlorine and bromine, although it is much less energetic. It bleaches, although slowly, and combines directly with hydrogen, chlorine, sulphur, phosphorus, and many of the metals. When a crystal of iodine is laid on a small piece of phosphorus the combination is attended with so much heat as to inflame the latter. As in the case of bromine, sodium and iodine can be heated together without change, while with potassium the action is explosively rapid.

With starch solution a trace of iodine forms a deep blue color. This color is destroyed on heating and reappears on cooling. The compounds of iodine do not produce this color with starch until a little chlorine is added to liberate the iodine ; an excess of chlorine destroys the color.

Uses.—Iodine is used extensively in the manufacture of some of the coal-tar colors, in the preparation of iodides, in photography, and in medicine.

Impurities and Tests.—Fixed impurities, as coal, plumbago, etc., may be recognized by volatilizing a small quantity of the sample, which should leave no residue. An excess of moisture is indicated by the iodine adhering to the sides of the bottle, and by it failing to form a perfectly clear, limpid solution with chloroform. *Iodine chloride* is detected on agitating a sample with water, to which not more than a yellowish-brown color should be imparted. Compounds of iodine with chlorine, bromine, and cyanogen may be detected by triturating one part of iodine with twenty parts of water and filtering the solution. To one-half of the solution carefully add decinormal sodium hyposulphite solution until the solution is just decolorized. Then add a few drops of ferrous sulphate solution, and subsequently a little sodium hydrate, and heat the mixture gently. On now adding a slight excess of hydrochloric acid, the liquid should not assume a blue color, indicating the absence of *iodine cyanide.* To the other half of the aqueous filtrate add a slight excess of silver nitrate solution, shake actively and allow the precipitate to subside, and, having poured off the clear supernatant liquid completely, shake the precipitate with a mixture of 1 c.c. of ammonia water and 9 c.c. of water, and filter. Upon the addition of a slight excess of nitric acid to the filtrate not more than a slight opalescence should make its appearance, indicating the limit of *chlorine* or *bromine.*

PRACTICAL EXERCISES.

(1) Pass chlorine into a dilute (about one per cent.) solution of potassium iodide; the liquid will become dark in color, owing to separation of iodine. In stronger solutions the iodine would be precipitated.

(2) To a portion of the iodine solution, diluted with water, add solution of starch; a blue color will form, due to the combination of starch with iodine. When a precipitate is formed instead of a blue color, it is an indication that the iodine solution is too strong, and a more dilute one must be used. The blue color of the starch iodide is destroyed by heat and by excess of chlorine.

(3) To another portion of the iodine solution in a test-tube add a small quantity of chloroform and agitate; the chloroform will remove the iodine from the water, and settle to the bottom of the tube as a deep violet-colored liquid, and the water above will become nearly colorless.

IODINE AND HYDROGEN.

HYDROGEN IODIDE. HYDRIODIC ACID.

Formula, HI. *Molecular Weight*, 127.53.

Preparation.—A mixture of equal volumes of hydrogen and iodine vapor, passed over platinized asbestos heated to redness, partly combines, forming hydrogen iodide. This reaction does not take place nearly so readily as in the case of hydrogen and chlorine, or even hydrogen and bromine; and the combination only imperfectly takes place when hydrogen is burned in iodine vapor.

As with hydrogen bromide, the method with amorphous phosphorus is the best for obtaining the gas in quantity. One part of amorphous phosphorus is mixed with fifteen parts of water in a suitable flask, and twenty parts of iodine are gradually added, keeping the flask cool, with ice if necessary, and allowing the action after each addition to cease before adding more. When all the iodine has been added, and action has finally ceased, gentle heat may be applied, and the gas, which is very heavy, collected by downward displacement. The same precautions of passing the gas over a mixture of amorphous phosphorus and broken glass may be observed here as with hydrogen bromide. Mercury is acted on by hydriodic acid gas, and, therefore, cannot be used for the collection. The reaction is as follows:

$$\underset{\text{Phosphorus.}}{P_4} + \underset{\text{Iodine.}}{6I_2} = \underset{\text{Phosphorus Tri-iodide.}}{4PI_3}.$$

$$\underset{\text{Phosphorus Tri-iodide.}}{4PI_3} + \underset{\text{Water.}}{12H_2O} = \underset{\text{Hydriodic Acid.}}{12HI} + \underset{\text{Phosphorous Acid.}}{4H_3PO_3}.$$

Another method, used when a solution of the gas in water is desired, consists in passing hydrogen sulphide into water containing iodine:

$$\underset{\text{Iodine.}}{2I_2} + \underset{\substack{\text{Hydrogen}\\\text{Sulphide.}}}{2H_2S} = \underset{\substack{\text{Hydrogen}\\\text{Iodide.}}}{4HI} + \underset{\text{Sulphur.}}{S_2}.$$

The small quantity of iodine in solution is first converted into hydrogen iodide, which in turn dissolves more iodine to be acted on. Sulphur is deposited at the same time, and to prevent it enclosing the iodine, it is preferable to agitate, and add the latter in small portions at a time. The solution must be boiled to separate the excess of hydrogen sulphide, and filtered to remove sulphur.

Hydrogen iodide may also be prepared by heating together phosphoric acid and potassium iodide:

$$\underset{\substack{\text{Potassium}\\\text{Iodide.}}}{3KI} + \underset{\substack{\text{Phosphoric}\\\text{Acid.}}}{H_3PO_4} = \underset{\substack{\text{Potassium}\\\text{Phosphate.}}}{K_3PO_4} + \underset{\substack{\text{Hydrogen}\\\text{Iodide.}}}{3HI}.$$

The use of sulphuric instead of phosphoric acid in this process is precluded on account of the reduction of the sulphuric acid, according to the following reaction:

$$\underset{\substack{\text{Potassium}\\\text{Iodide.}}}{2KI} + \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{3H_2SO_4} = \underset{\substack{\text{Acid}\\\text{Potassium}\\\text{Sulphate.}}}{2KHSO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\substack{\text{Sulphur}\\\text{Dioxide.}}}{SO_2} + \underset{\text{Iodine.}}{I_2}.$$

Properties.—Hydrogen iodide is a colorless, heavy gas, with a sharp, irritating odor, and an acid taste and reaction. At 0° and a pressure of four atmospheres it forms a colorless liquid, which solidifies at —51°. Its specific gravity is 4.41. The gas is very soluble in water, and when saturated at 0° the solution has a specific gravity of 1.99.

Both the strong and weak solutions vary in boiling point until the strength of 57.75 per cent. is reached, when it distils at 127°, under ordinary atmospheric pressure. The gas commences to decompose at 180°, and if some of it be poured down on the flame of a Bunsen burner, clouds of iodine vapor are evolved. It also readily decomposes when a red-hot platinum wire is plunged into a vessel of it, or more slowly when simply exposed to the air. This accounts for the difficulty of preparing the gas by the direct union of the elements. The aqueous acid readily decomposes on exposure to light, and becomes dark brown in color; for this reason a syrup of it has been made official, instead of the acid of 1860, in order to take advantage of the preservative action of sugar.

Uses.—The acid has some use in medicine, and is also much employed in chemical operations where a reducing agent is desired, on account of the readiness with which it is decomposed, giving hydrogen in the nascent state.

Iodides.—These salts, like the bromides, may be prepared from the acid, but it is cheaper to make them directly from the element. They are nearly all soluble in water, the important exceptions being the silver, mercurous, mercuric, and lead iodides. Heat fuses and decomposes the iodides, with formation of the metal or its oxide and free iodine.

Detection.—The acid and its salts are detected by the addition of starch and chlorine water, when, if the starch solution be sufficiently dilute and the chlorine in not too great excess, there will be formed the blue starch iodide. This blue color disappears on heating and reappears on cooling, and is destroyed by an excess of chlorine water. When the blue mixture is agitated with ether, chloroform, or carbon disulphide, the iodine is withdrawn, imparting to the solvent a red or violet color, according to the amount present. Before deciding finally on the presence of hydriodic acid and iodides, one must be sure that such salts as the sulphites and thiosulphates are either absent or are completely oxidized by the chlorine, for the blue color will not appear until all readily oxidizable substances are converted. A few organic substances, notably tannin, interfere with the formation of the blue color. When bromides are present with iodides, the color resulting from the addition of starch and chlorine water will be green, from a mixture of the yellow starch bromide with the blue starch iodide.

IODINE AND CHLORINE.

These two elements unite in two proportions, forming iodine monochloride, ICl, and iodine trichloride, ICl_3. The former is prepared by passing dry chlorine over dry iodine, until the latter is liquefied, or by distilling one part iodine with four parts potassium chlorate, or by boiling iodine with strong aqua regia, diluting with water, and agitating with ether. The ether dissolves the iodine chloride, and leaves it behind on evaporation. It is a thick, reddish-brown liquid, which solidifies, on standing, to well-defined crystals, which melt at 24.7°. It is decomposed by water, forming iodic acid, hydrochloric acid, and free iodine. As might be expected, it does not color solution of starch, on account of the presence of chlorine.

Iodine trichloride is prepared by continuing the passing of chlorine over the iodine monochloride until a solid compound is obtained. This is a solid, crystalline compound, of a yellow color, which, when heated to 25°, gives off chlorine, forming the monochloride. It partly dissolves in water, and is in part decomposed into iodic and hydrochloric acids and free iodine. A solution is prepared for medicinal use by suspending 5.5 grammes of iodine in 22 grammes of water, and passing in chlorine as long as it is absorbed by the well-cooled mixture.

The solution contains 10 grammes of iodine trichloride.

For testing, the aqueous solution (1 to 20) is agitated with chloroform, which must not be colored violet at once, but the color should appear immediately on the addition of a few drops of stannous chloride.

FLUORINE.

Symbol, F. *Atomic Weight*, 19. *Valence*, I.

History.—In the latter part of the eighteenth century, Marggraf noticed that his retort was powerfully attacked when he heated in it a mixture of fluor-spar and sulphuric acid. Ampère, in 1810, pointed out the analogy between hydrochloric acid and the compound at that time called fluoric acid; hence, when adapted to more modern nomenclature, the name of this peculiar compound became hydrofluoric acid.

Many attempts have been made in recent years to isolate the element. Its action on the vessels containing it and its intense affinity for moisture prevented its separation in the free state in such a quantity and degree of purity as to be of any value.

In 1886, Moissan, by passing a powerful electric current through anhydrous hydrofluoric acid, liquefied at 0° and cooled to —23°, and contained in a U-shaped tube of platinum, succeeded in obtaining the free element as a colorless gas. A small quantity of potassium fluoride was added to the acid to make it a better conductor, and the positive pole, at which the element appeared, was an alloy of platinum and iridium. The platinum tube in which the operation was carried out was not acted on perceptibly at such a low temperature.

Occurrence.—Fluorine is said to occur in the free state in the crevices of certain fluor-spar deposits in Bavaria. It is, however, only in minute quantity and recognized by its odor. It occurs combined in a number of minerals, chiefly as calcium fluoride or fluor-spar, CaF_2, and as sodium and aluminum fluoride or cryolite, $6NaF.Al_2F_6$. The former of these is pretty well distributed over the globe, the latter is found in Greenland. Fluorine has been found in small quantity in sea water, in many mineral waters, in the bones and teeth of man, and in milk.

Preparation and Properties.—The preparation has been sufficiently described under its history. Fluorine is a colorless gas, with an odor resembling hypochlorous acid. It is the most powerful of all the known elements; gold, platinum, with, perhaps, a few other of the noble metals, and oxygen are not attacked by it. It combines explosively with hydrogen in the cold, and decomposes the alkali chlorides, when they are anhydrous, liberating chlorine. Water is decomposed by it, with formation of hydrogen fluoride and ozone. Cork chars and ignites in the gas, and many organic substances, like benzene, alcohol, and turpentine, are inflamed on coming in contact with it. Its rapid action on many metals at ordinary temperatures is prevented by the formation of a coating of fluoride; iron, however, completely absorbs it. Hydrogen, sulphur, phosphorus, iodine, arsenic, antimony, silicon, boron, potassium, and sodium combine with it on contact with great energy, attended with heat and light.

FLUORINE AND HYDROGEN.

HYDROGEN FLUORIDE. HYDROFLUORIC ACID.

Formula, HF. *Molecular Weight*, 20.

Preparation.—The pure anhydrous acid is prepared with considerable difficulty by heating the acid potassium fluoride in a platinum retort, connected with a condenser and receiver of the same metal. The principal difficulties arise from moisture, and from danger of inhaling the vapor, which is extremely irritating and poisonous. Sulphur has been used as a lute in making tight joints.

The diluted acid is more easily prepared from fluor-spar and sulphuric acid, in a leaden or platinum vessel. The vapor is conducted through a tube of the same metal into water in a lead, platinum, or gutta-percha vessel:

$$\underset{\text{Calcium Fluoride.}}{CaF_2} + \underset{\text{Sulphuric Acid.}}{H_2SO_4} = \underset{\text{Calcium Sulphate.}}{CaSO_4} + \underset{\text{Hydrogen Fluoride.}}{2HF.}$$

The pure anhydrous acid is a colorless liquid, having a specific gravity of 0.9879 at 13°. It boils at 19.4°, and at —102.5° solidifies to a crystalline mass which melts at —92.3°. Hydrogen fluoride does not act on glass as long as it is absolutely free from moisture, and the non-metals are but slightly affected by it. It is very soluble in water, and the solution is understood in speaking of hydrofluoric acid. The most concentrated solution has a specific gravity of 1.25, and this on heating gives off the gas until the specific gravity is reduced to 1.15, when it distils unchanged at 120°, and contains 36 to 38 per cent. of the anhydrous acid. The aqueous acid rapidly attacks glass, combining with the silica as follows:

$$\underset{\text{Hydrogen Fluoride.}}{4HF} + \underset{\text{Silicic Oxide.}}{SiO_2} = \underset{\text{Silicon Fluoride.}}{SiF_4} + \underset{\text{Water.}}{2H_2O.}$$

On account of this property, one of the most important uses of the acid is in etching glass. That portion of the glass to be preserved from its action is covered with a film of wax or paraffin dissolved in turpentine oil. The divisions on thermometers, eudiometers, and other graduated apparatus are marked with its aid. The dilute commercial acid is transported in wooden vessels, and the more concentrated article in gutta-percha or paraffin (ceresin) bottles.

At a temperature of 30°, the density of hydrogen fluoride is such as to lead to the conclusion that, at that point and below, it exists as the double molecule, H_2F_2. Above that temperature it possesses the formula HF. This view is supported by the fact that some of its salts are acid in character; that is, only half of the hydrogen of the acid is replaced by a base, for instance, the one with potassium, used in its preparation, has the formula KHF_2.

CHAPTER IV.

THE OXYGEN GROUP.

OXYGEN.

Symbol, O. *Atomic Weight*, 15.96. *Valence*, II.

History.—Oxygen was discovered by Priestley, of England, August 1, 1774, and a short time after, independently, by Scheele, of Sweden. Lavoisier gave it the name *oxygenium*—acid-former—under the impression that to it were due the acid properties of many bodies.

Occurrence.—Although oxygen does not occur alone and uncombined, it does exist in the atmosphere in the free state, mixed with four volumes of nitrogen.

In combination it occurs still more abundantly, eight-ninths of the water in the globe being composed of it, and it exists in large percentage in nearly all mineral substances. The statement has been made that one-half of the solid part of the earth is composed of this element. In combination with carbon and hydrogen, it forms the basis of nearly all the organic compounds in the vegetable kingdom.

Preparation.—(1) The original method of preparing oxygen, by heating mercuric oxide, as discovered by Priestley, is still useful for illustration:

$$2HgO = 2Hg + O_2.$$

(2) By heating a nitrate, as potassium nitrate:

$$2KNO_3 = 2KNO_2 + O_2.$$

(3) By the electrolysis of water:

$$2H_2O = 2H_2 + O_2.$$

(4) By heating manganese dioxide and sulphuric acid:

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$

(5) When potassium dichromate and sulphuric acid are mixed, chromium trioxide is formed, according to the following reaction:

$$K_2Cr_2O_7 + 2H_2SO_4 = 2KHSO_4 + H_2O + 2CrO_3.$$

On heating this mixture with an excess of sulphuric acid, oxygen is liberated:

$$2CrO_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O + O_3.$$

(6) On heating an aqueous solution of bleaching powder—calcium hypochlorite—and cobaltous chloride to 70° or 80°, cobaltous oxide is formed, which in reacting on the calcium hypochlorite is converted into cobaltic oxide, and this in turn gives up oxygen:

$$Ca(ClO)_2 + 4CoO = CaCl_2 + 2Co_2O_3.$$
$$2Co_2O_3 = 4CoO + O_2.$$

(7) The method most used on a small scale at the present time consists in heating a mixture of four parts potassium chlorate and one part manganese dioxide. The action of the latter is either mechanical or catalytic, as the chlorate will yield oxygen when heated alone, provided the temperature is raised to 325°, and then slowly higher. The object of the mixture, however, is to obtain the gas at the lower temperature of 200°, and without fusion of the chlorate:

$$2KClO_3 = 2KCl + 3O_2.$$

This method is usually carried out in a copper or iron retort, with arrangements for feeding in about one pound of the mixture at a time, without disconnecting.

Every new lot of manganese dioxide should be tested, by heating a small quantity in a test-tube with some chlorate, in order to prove the absence of impurities of an organic character, which, if present, would cause an explosion when heated.

(8) A number of processes have been proposed for preparing oxygen on a larger scale and at a lower cost than is possible by the preceding. One of these, suggested by Deville and Debray, consists in allowing sulphuric acid to trickle into a retort filled with bricks and heated to redness. The decomposition takes place as follows:

$$2H_2SO_4 = 2SO_2 + 2H_2O + O_2.$$

The sulphur dioxide is removed by passing the mixture of gases through water, or up through a tower filled with coke, over which a small stream of water trickles. The sulphur dioxide may be utilized by converting it into sulphuric acid to be used again.

(9) The Tessie du Motay method suggests the heating of potassium or sodium manganate in a current of steam. The details

of the process are the formation first of the manganate from manganese dioxide and sodium hydrate heated to 450° to 500° in a current of air:

$$2MnO_2 + 4NaOH + O_2 = 2Na_2MnO_4 + 2H_2O.$$

It is then heated to low redness and steam passed over the mass, when the reverse action sets in with formation of the original materials:

$$2Na_2MnO_4 + 2H_2O = 2MnO_2 + 4NaOH + O_2.$$

This process is one of a number that have been designed to use the atmosphere as the source of oxygen, and thereby furnish a large amount of the gas at a very small expense. In this particular case, however, the manganese salt deteriorates each time it is heated, and finally ceases to act altogether.

(10) Brin's process also consists in extracting the oxygen from the atmosphere. It was patented in 1880, and again in 1885, but still required the improvements of three or four years to bring it to a successful condition on a large scale. The principle involved is not new, having been proposed by Boussingault. It has long been known that many peroxides, notably that of barium, give up their oxygen at high temperatures, and regain it from the atmosphere on cooling.

The Brin process, as now perfected, consists in heating a porous barium oxide to 700° in closed vertical retorts, into which purified air is forced under a pressure of ten or fifteen pounds in excess of that of the atmosphere. The barium rapidly undergoes peroxidation, and, as soon as complete, the air-pressure is reduced to fourteen pounds below the atmospheric pressure, when oxygen is rapidly given off. The whole time occupied in the oxidation of the barium and in the recovery of the gas is said not to exceed ten minutes. One of the important conditions of this process is to have the barium oxide in a porous condition. This is attained by heating barium nitrate to 880° for three or four hours. Another condition is the use of pure air,—that is, free from carbon dioxide. This is accomplished by a system of washers containing lime and sodium hydrate. The oxygen obtained has a purity of from 90 to 96 per cent., and is conveyed into a large gas-holder, from which it is pumped into steel cylinders under a pressure of 800 to 1000 pounds, in which form it goes into commerce. The small cylinders contain forty gallons of the gas compressed to about the volume of one-half gallon.

Properties.—Oxygen is a colorless, odorless, and tasteless gas. It is slightly soluble in water, 100 volumes of the liquid at 0° dissolving 4.1 volumes of the gas. The specific gravity of oxygen is 1.10563 (air = 1), and its density 15.96. Under a pressure of 22.5 atmospheres and at a temperature of —136°, it liquefies, and in that condition it has a specific gravity of 0.899 (water = 1). This liquid is colorless and boils at —184° under a pressure of one atmosphere. It is also distinctly magnetic; taking the magnetism of iron at 1,000,000, that of oxygen becomes 377.

In chemical properties oxygen is very active, combining either directly or indirectly with all the known elements except fluorine. It is not a combustible gas under ordinary circumstances, but it supports the combustion of many elements and compounds. The term combustibility is considered to refer to the power of a substance to continue burning in the air after being once ignited; that is, to combine with the oxygen of the atmosphere. When mixed with hydrogen the two explode violently on the application of flame or the electric spark, the result of the combination being water. With many other of the elements oxygen unites at ordinary temperatures, sodium, potassium, and phosphorus being examples; with others again, as sulphur, iron, carbon, and copper, an elevated temperature is required, while with platinum, gold, and silver, combination does not take place at any temperature. The products of these combinations are called *oxides*, those with the non-metals being *acid-forming oxides;* that is, capable of forming acids by combination with water, while most of those with metals are *basic oxides*, many of which form basic hydrates with water.

A great number of the compounds with which we will deal later are combinations of oxygen with some other element. As examples of the formation of oxides we may take the following:

$Zn + O = ZnO$, Zinc oxide.
$C + O_2 = CO_2$, Carbon dioxide.
$P_2 + O_5 = P_2O_5$, Phosphoric oxide.
$Fe_3 + O_4 = Fe_3O_4$, Ferroso-ferric oxide.

All of these elements burn brilliantly in oxygen when once ignited; this is accomplished in the case of zinc and iron by attaching the glowing end of a match, and with phosphorus and carbon by bringing them in contact with flame a moment before introducing into the gas. In the act of respiration a chemical process is involved, whereby certain organic constituents of the blood are consumed, with formation of carbon dioxide and water.

Uses.—The low cost at which oxygen can be produced by the Brin process has admitted of its application in a number of operations from which it has heretofore been excluded. Except in the nascent state, oxygen alone appears to have no bleaching action, but it has been found that a small proportion added to a solution of bleaching powder greatly increases the efficiency of the latter. In aging spirits, the gas has been found effective when forced into the liquid under a pressure of one or two atmospheres, and to accomplish in a short time what usually requires years by the ordinary method. It has also been found to assist in the removal of sulphur from illuminating gas when mixed with the latter previous to its passage over the lime. Oxygen gas when properly associated with hydrogen, or illuminating gas, is used in certain metallurgical operations where a high temperature is required, and for furnishing a brilliant light, as in the oxyhydrogen lantern. Although frequently tried, the use of oxygen in medicine has not been attended with very encouraging results.

PRACTICAL EXERCISES.

(1) Prepare oxygen by placing a few crystals of potassium chlorate in a clean dry test-tube, adapt a delivery-tube long enough to reach under the surface in a vessel near by. Apply a steady flame, taking care not to allow any water to be drawn back into the tube; this may be accomplished by taking the end of the delivery-tube from the water before the flame is withdrawn. As soon as bubbles of gas escape freely, and the air has been expelled, bring a test-tube filled with water over the escaping gas and collect it.

The evolution of oxygen is effected more easily by mixing with the potassium chlorate, before heat is applied, about one-fourth its weight of manganese dioxide.

(2) Apply a lighted taper to a tube full of oxygen, the gas will not burn. Plunge the taper into the gas and it will burn with greatly increased energy. Extinguish the flame, leaving a glowing spark, and again plunge into the gas, the taper will be re-ignited. These experiments indicate the non-combustibility of oxygen under ordinary circumstances, but show that it is an active supporter of combustion.

(3) A piece of glowing charcoal is lowered into the gas; a rapid combustion ensues and the charcoal disappears. Pour some lime water into the tube, agitate well; a white precipitate of calcium carbonate is produced. If this be tried with oxygen, previous to the burning of the charcoal, no precipitate will be formed. A number of other substances, as phosphorus, sulphur, and iron, will, when once ignited, burn in oxygen with great brilliancy.

(4) Take two test-tubes, one about twice the capacity of the other. Fill the larger with hydrogen and the smaller with oxygen, bring their mouths together and, after turning once or twice to thoroughly mix their contents, open their mouths to a flame. A sharp report is caused by the combination to form water. If more than two volumes of hydrogen to one of oxygen be present, the surplus remains uncombined; if oxygen be present in greater proportion, the excess of it remains.

OZONE.

Formula, O_3. *Molecular Weight*, 47.88.

History.—This peculiar substance was first noticed by Van Marum, in 1785, in passing electric sparks through oxygen, of which it appears to be only a modification. Schönbein, in 1840, gave it the name *Ozone*, from Greek ὄζω, signifying "I smell."

Occurrence.—Ozone is found in minute quantities in the atmosphere which is remote from large cities, and is especially noticeable after a thunder-storm. It is also supposed to be produced by the growth of plants.

Preparation.—(1) Ozone is evolved at the positive pole in the electrolysis of water acidified with sulphuric and chromic acids. (2) It is also formed by the silent discharge of electricity through air or oxygen. For this purpose a Siemens' ozonizing tube is employed. (3) When phosphorus is allowed to slowly oxidize in the air. This is best accomplished by standing two or three sticks of phosphorus on end in a dish containing a shallow layer of water, so that they are about one-half immersed in the liquid. A stoppered bell-jar is then placed over the whole, and very soon ozone may be detected by the appropriate tests.

It is difficult to obtain a definite volume of ozone, since it is always mixed with air or oxygen, but it may be accomplished by passing the mixture of ozone and oxygen from a Siemens' apparatus through a tube cooled with liquid oxygen to —181°, when the ozone separates as a steel-blue liquid, boiling at —106°.

Properties.—Ozone is a colorless gas with a peculiar, irritating odor. It possesses very active oxidizing powers, attacking most organic matter, and oxidizing many of the metals, like mercury and silver. It liberates iodine from potassium iodide, and this property is turned to account in the following test: Paper is saturated with solutions of potassium iodide and starch, and then dried. This paper becomes blue in the presence of a trace of ozone. Of course, chlorine and the higher oxides of nitrogen must be avoided.

At a temperature of 237° ozone is converted into ordinary oxygen; this change takes place, though slowly, at much lower temperatures.

Composition.—It has been shown in several ways that ozone is an allotropic form of oxygen, in which three atoms combine to form a molecule instead of two; consequently, in its formation three volumes of oxygen condense and form two volumes of ozone.

The preparations known as "ozonized water," "pyrozone," are mainly solutions of hydrogen peroxide (see p. 174).

Uses.—Various uses have been suggested for ozone, chiefly in the industrial process of bleaching. It has also been used as a disinfectant and somewhat as an oxidizing agent in industrial processes.

OXYGEN AND HYDROGEN.

These elements combine in two proportions:

Hydrogen monoxide, or Water,	H_2O.
Hydrogen dioxide,	H_2O_2.

WATER.

Formula, H_2O. *Molecular Weight*, 17.96.

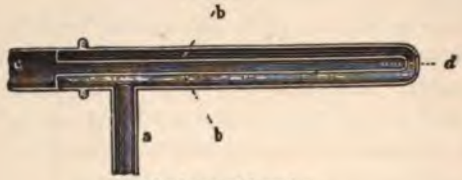
History.—When Cavendish, in 1766, discovered hydrogen, it opened the way for breaking down the ancient belief in the elementary nature of water. This he followed up by exploding a mixture of hydrogen and air with the electric spark, and suggesting that hydrogen and oxygen, in the proportions of two volumes of the former and one of the latter, combine to form water. This was confirmed by Lavoisier, in 1783, who decomposed water into its elements and decided that it was composed of one part, by weight, of hydrogen, and eight parts, by weight, of oxygen. Gay-Lussac and Humboldt, in 1805, confirmed these experiments and those of Cavendish.

Occurrence.—In addition to the abundant natural occurrence, as we are accustomed to see it, water is very widely distributed in such a way as to escape casual observation. All plants and animals contain it in large amount, and considerable quantities exist in the atmosphere.

Formation.—The simplest method of forming this compound from its elements, hydrogen and oxygen, and proving the product to be water, is to burn a jet of hydrogen in air, and hold over the flame a cool bell-jar, which will immediately become coated with a film of moisture. When a mixture of the two gases is brought in contact with flame, a violent explosion results. If, however, they are brought together at the moment of their combination, so as to prevent explosion, the mixture will burn with a very intense heat. The apparatus by which this is accomplished is illustrated in Fig. 48, and it is known as the oxyhydrogen blowpipe. The hydrogen is introduced through the tube *a* and ignited at *d*; oxygen is then introduced through *c*. When the jet is directed against a piece of freshly-burned lime, we have the oxyhydrogen lamp, the incandescent lime of which gives an intense light.

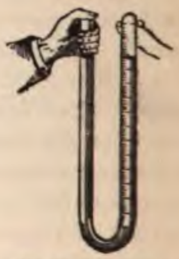
Synthesis.—The synthesis of water is accomplished by the use of Ure's eudiometer tube, Fig. 49. The tube, having been filled with water or mercury, is connected with an oxygen supply and a definite amount of this gas run into the closed limb; in the same manner twice as much hydrogen is introduced, the measurements being made with the columns of liquid in the two limbs at exactly the same height. A small air-space is left in the open end of the tube to act as a cushion. The aperture is then tightly closed with the thumb, and an electric spark passed through the mixed gases, by means of the platinum wires, which are fused into the closed end. A slight flash appears on the passage of the spark, and immediately suction is felt by the thumb. On removing the latter carefully, and filling the open limb with the additional amount of water necessary, the gases in the closed limb will be found to have disappeared. It is, perhaps, more striking to explode equal volumes of the two gases, when it will be found that a quantity equal to one-half of the oxygen introduced remains, which may easily be proved to be that gas by applying a glowing taper.

FIG. 48.



Oxyhydrogen blowpipe.

FIG. 49.



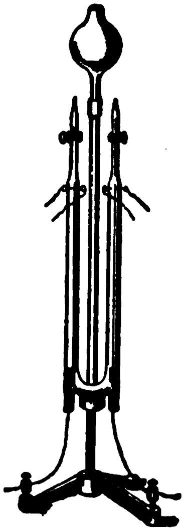
Ure's eudiometer.

Analysis.—For the purpose of determining the composition of water by analysis, the apparatus illustrated in Fig. 50 is best adapted. The tubes are filled with water, to which a little sulphuric acid has been added to make the liquid a better conductor of electricity. On attaching the wires from the opposite poles of a battery of two or more cells, a steady current of the two gases will rise in the two closed limbs of the apparatus. It will be found, on testing, that one of these gases, that from the negative electrode, will burn and otherwise respond to the tests for hydrogen, while the other, from the positive electrode, will ignite a glowing taper and show the other tests for oxygen. The hydrogen, it will also be noticed, occupies just twice the space filled by the oxygen.

Properties.—Pure water is an odorless and tasteless liquid. In small quantities it is colorless, but in larger volume it has a bluish color. On cooling the water to 0°, it solidifies, or, rather, crystallizes, in the hexagonal system; on the application of heat, it boils at 100° under the ordinary atmospheric pressure of 760 millimeters of mercury. Water, at a certain temperature, affords an exception to the rule that bodies expand with heat and contract on cooling. At 4° it reaches its greatest density, and below, to the solidifying point at 0°, it expands. On account of this peculiar property, ice floats on water instead of sinking, as it otherwise would.

The specific gravity of water at its greatest density, 4°, is 1.000, and at 0° it is 0.99987. The melting temperature of ice is quite constant, but under certain conditions, for instance, under pressure, the freezing may not take place until several degrees below zero have been reached. The boiling point of water bears a constant relation to the pressure. Under one atmosphere (the ordinary pressure) the boiling point is constant: the application of more heat only causes the liquid to boil faster, but does not increase its temperature. When, however, the liquid is confined under a pressure of two atmospheres, the temperature will rise on the application of heat to 120.6°, when boiling will commence.

FIG. 50.



Electrolytic decomposition of water.

The following table gives the temperature at which water boils under an increase of pressure:

Pressure in atmospheres.	Boiling point.	Pressure in atmospheres.	Boiling point.
1	100°	6	159°
2	120.6°	8	170.8°
3	133.9°	10	180.3°
4	144°	25	224.7°

Below the ordinary boiling point of water the pressure is best expressed in millimeters of mercury, as follows:

Pressure in millimeters of mercury.	Boiling point.	Pressure in millimeters of mercury.	Boiling point.
760.000	100°	17.391	20°
525.450	90°	12.699	15°
354.280	80°	9.165	10°
233.093	70°	6.534	5°
148.791	60°	4.600	0°
91.982	50°	2.093	—10°
54.906	40°	0.927	—20°
31.548	30°		

Water combines with many bodies with considerable energy. Of these the most striking are certain basic oxides, as potassium oxide, K_2O, and calcium oxide, CaO, which form hydrates as follows:

$$K_2O + H_2O = 2KOH,$$
$$CaO + H_2O = Ca(OH)_2.$$

With certain acid oxides it combines energetically to form acids, as follows:

$$SO_3 + H_2O = H_2SO_4,$$
$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

In all these cases considerable heat is developed.

Water is a very stable compound, withstanding a temperature of 1000°; above this point, dissociation takes place. Some elements, like potassium or calcium, decompose it with evolution of hydrogen:

$$K_2 + 2H_2O = 2KOH + H_2.$$

Some metals decompose it at the ordinary temperatures without exhibiting much energy in the form of heat; this, however, is due to the extreme slowness of the action.

Water enters into the composition of many bodies as *water of crystallization*, some in a remarkable degree, as sodium phosphate, $Na_2HPO_412H_2O$, which at 100° loses all its water, amounting to 60.30 per cent., and alum, $K_2Al_2(SO_4)_424H_2O$, which at 200° loses all its water, amounting to 45.52 per cent.

Water comes nearer than any other liquid to being a universal solvent, for which purpose, on account of its stable nature, it is especially adapted.

The foregoing description refers to a pure water as prepared by distillation, but water may be further considered under the following different varieties:

Distilled water.
Rain water.
Spring and mineral waters.
Sea water.

(1) **Distilled Water.**—Ordinarily the distillation of this liquid is accomplished by boiling a good, natural water and passing the vapor into a block tin or glass condenser. The first portions which come over contain certain gases and should be rejected; then a quantity amounting to about 80 per cent. of the whole should be collected in glass-stoppered bottles and preserved for use. The residue in the still contains the solid impurities, and should be washed out before another portion of water is put in. When thus prepared, distilled water should possess the physical and chemical properties previously described, and should leave no residue when one liter is evaporated in a porcelain or platinum dish.

Tests.—The following tests, in addition to the evaporation of some of the liquid as above described, would prove the absence of all probable impurities. A few drops of lead acetate solution should produce only a faint turbidity, and when another portion is mixed with an equal volume of calcium hydrate solution no cloudiness should appear, showing the absence of carbonic acid. No turbidity should develop, after some hours' standing, with a small quantity of barium chloride solution,—absence of sulphuric acid. No opalescence should appear on addition of silver nitrate,—absence of chlorine. Nitric acid may be detected by mixing ten to twenty parts of the water with one or two parts of concentrated sulphuric acid and one drop of indigo solution; the blue color should not disappear on heating to 100°. From 10 to 20 c.c. of the water should give only a faint yellowish color with five drops of Nessler's reagent (potassio-mercuric iodide), indicating the absence of ammonia compounds. Organic matter may be detected by adding to 100 c.c. of the water 1 c.c.

of concentrated sulphuric acid, heating to 100°, and adding a few drops of a dilute solution (1–100) of potassium permanganate, when the red color imparted by the latter should not be destroyed after some hours' standing in a well-closed vessel.

(2) **Rain Water.**—This is the purest form of natural water, provided it can be collected without contamination. Under ordinary circumstances it becomes impure from the atmospheric gases, especially in the vicinity of large cities; of these, carbon dioxide is the most abundant, although sulphurous oxide is also present in considerable quantity. Rain water is usually collected from roofs, on which there is ordinarily more or less dust and other foreign matter; this renders the water impure, unless the first portions that fall can be run off and rejected. When properly collected, rain water is one of the most satisfactory for washing purposes, but is rather unpalatable for drinking.

(3) **Spring Water.**—The water-supply of cities is usually taken from lakes or rivers, while that in country districts is taken from wells or springs. The water from these sources, having been in contact with the earth, holds in solution small quantities of mineral compounds, frequently calcium sulphate or carbonate, with varying amounts of organic matter. The fitness of a water for domestic purposes is usually determined by the amount of organic matter present, and more exactly by an estimation of the nitrogen of this organic matter. The water from the large lakes is considered purest, while that from rivers is often quite impure on account of sewage contamination from sources higher up the stream. Water from wells in cities should never be used for domestic purposes unless it is taken from a bored well, cased in and of such depth as absolutely to insure its freedom from surface drainage.

After the freedom of a water from organic matter has been established, the question of *hardness* is still an important factor in determining its value for domestic purposes. When calcium and magnesium salts are present in a water they form insoluble precipitates with soap, which are inconvenient in washing; such a water is called *hard*, and requires the use of a great deal more soap in order to produce lather. These salts are usually sulphates or carbonates, frequently both, the latter being held in solution by the carbon dioxide present. When the hardness is due to sulphate, it is said to be *permanently hard*, in distinction from that which contains carbonates held in solution by carbon dioxide, which is termed *temporarily hard.* In the latter case it becomes a soft water by simply boiling, which drives off the carbon dioxide and precipitates the salts as carbonates. Water is said to have one degree of hardness when it contains one part of calcium carbonate or its equivalent in one hundred thousand. The degree of hardness is determined by agitating the sample of water with a standard solution of soap until a permanent lather is produced. The standard solution of soap is prepared by agitation with calcium chloride solution of known strength. "Each degree of hardness indicates the destruction and waste of twelve parts of the best hard soap by one hundred thousand parts of water." (Frankland.)

Mineral Waters may be considered a class of spring waters, since they are found either in springs or wells. When a water contains so much mineral or gaseous matter as to render it unfit for domestic use, it usually becomes more or less valuable for medicinal purposes. Such waters are often designated by the character of their most important medicinal constituent. Therefore we have the following varieties:

Carbonated waters, which contain carbon dioxide in considerable quantity, often holding in solution calcium and magnesium carbonates. Such waters often effervesce on coming to the surface. The Waukesha water, from Waukesha, Wisconsin, is an example of this class.

Sulphur waters contain hydrogen sulphide, and deposit sulphur on exposure to the atmosphere. Sometimes both sulphuretted hydrogen and carbon dioxide are present in the same water. Richfield Springs, New York, and White Sulphur Springs, West Virginia, belong to this class.

Alkaline waters usually contain considerable quantities of sodium bicarbonate with the sulphates of sodium and magnesium. The Apollinaris water of Neuenahr, Prussia, and the Capon Springs, West Virginia, are examples of this class.

Lithia waters frequently do not contain any notable amount of mineral substance, but include small quantities of lithium carbonate or chloride. The Vichy water from Vichy, France, is an example.

Saline waters contain relatively large proportions of magnesium and sodium sulphates with sodium chloride. The waters of Saratoga Springs, New York, and of Kissingen, Bavaria, are examples of general saline waters. Those of Carlsbad, Bohemia, and Bedford, Pennsylvania, are special magnesium waters.

Siliceous waters contain small quantities of alkaline silicates, and are represented by the hot springs of the Yellowstone Park and Iceland.

Chalybeate waters have iron as a constituent held in solution by carbon dioxide, and consequently deposit iron as a hydrate or oxide on exposure to the atmosphere. The waters of Pyrmont, Germany, and numerous American springs belong to this class.

A number of saline waters are so rich in certain chemical compounds as to constitute an important source of these substances, notable examples being the salt-wells of Pennsylvania, Ohio, and West Virginia, whose waters furnish sodium chloride, bromine, and iodine.

4. **Sea Water.**—This water contains on an average 3.50 per cent. of mineral substance. Sodium chloride constitutes 2.64 per cent., and the remainder consists chiefly of magnesium chloride and sulphate and calcium sulphate. The specific gravity of sea water is 1.02721 at zero.

HYDROGEN DIOXIDE.

Formula, H_2O_2. *Molecular Weight*, 33.92.

History and Preparation.—In 1818, Thénard, on treating barium dioxide with diluted hydrochloric acid, obtained this compound according to the following reaction:

$$\underset{\substack{\text{Barium}\\ \text{Dioxide.}}}{BaO_2} + \underset{\substack{\text{Hydrochloric}\\ \text{Acid.}}}{2HCl} = \underset{\substack{\text{Barium}\\ \text{Chloride.}}}{BaCl_2} + \underset{\substack{\text{Hydrogen}\\ \text{Dioxide.}}}{H_2O_2}.$$

It may also be prepared by passing a stream of carbon dioxide into water, and adding barium dioxide in small quantities at a time:

$$\underset{\substack{\text{Barium}\\ \text{Dioxide.}}}{BaO_2} + \underset{\substack{\text{Carbon}\\ \text{Dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Barium}\\ \text{Carbonate.}}}{BaCO_3} + \underset{\substack{\text{Hydrogen}\\ \text{-Dioxide.}}}{H_2O_2}.$$

Hydrogen dioxide is formed when a jet of burning hydroge impinges on the surface of water. A portion of the product dissolved in the liquid. In the preparation of hydrogen dioxi on a large scale, hydrofluoric acid is employed:

$$\underset{\substack{\text{Barium}\\ \text{Dioxide.}}}{BaO_2} + \underset{\substack{\text{Hydrofluoric}\\ \text{Acid.}}}{2HF} = \underset{\substack{\text{Barium}\\ \text{Fluoride.}}}{BaF_2} + \underset{\substack{\text{Hydrogen}\\ \text{Dioxide.}}}{H_2O_2}.$$

The barium fluoride, being insoluble, is allowed to subside, a the supernatant liquid, when decanted, is ready for use. T strengths, according to the volume of oxygen that a certain volume of the solution will yield. That in which one volume will yield ten volumes of the gas is, perhaps, most in demand.

The solution rapidly deteriorates on exposure to air and sunlight, and various methods have been adopted for preserving it. The decomposition is more rapid in alkaline solution. In some cases it is preserved with boric acid and glycerin.

Tests.—One of the readiest methods of detecting hydrogen dioxide is by the use of a paper moistened with solutions of potassium iodide and starch. It has been proposed to use this paper for quantitative purposes, by noting the depth of color and comparing with that produced on a similar paper which has been acted on by a solution of known strength. The special value of this test is that the reaction takes place in the presence of ferrous sulphate. Other oxidizing agents have the power to liberate iodine from potassium iodide, but not in the presence of ferrous sulphate. Another qualitative test consists in acidifying the solution slightly with sulphuric acid, adding ether, then a few drops of potassium chromate solution, and agitating the mixture. A blue color is developed, and, on allowing to stand, the ether separates as a deep-blue layer, the color of which is due to perchromic acid.

One of the best known methods of quantitatively determining hydrogen dioxide is based on the following reaction with potassium permanganate:

$$K_2Mn_2O_8 + 3H_2SO_4 + H_2O_2 = K_2SO_4 + 2MnSO_4 + 4H_2O + 3O_2.$$

A standard solution of the permanganate is run into a definite quantity of the dioxide solution until a permanent pink color is produced. Every molecule of the permanganate used represents one molecule of the hydrogen dioxide; or the permanganate may be added in excess and the volumetric solution of oxalic acid run in until the pink color disappears.

Another process that has been used with considerable success consists in measuring the volume of oxygen evolved when hydrogen dioxide and bleaching powder solution are mixed. One-half of the oxygen evolved comes from the hydrogen dioxide, according to the following reaction:

$$Ca(OCl)_2 + 2H_2O_2 = CaCl_2 + 2O_2 + 2H_2O.$$

[illegible]

Three [illegible]

Chlorine m[illegible]
Chlorine [illegible]
Chlorine pe[illegible]

Chlorine [illegible] above [illegible]

It will [illegible] from the [illegible] ducing [illegible]

[illegible]

No acid [illegible] sponding [illegible]

[illegible]

Preparation.—[illegible] rine through [illegible] dry precipitated [illegible] perature:

[illegible]

The gas [illegible] mixture, where it liquefies.

Properties.—[illegible] odor resembling [illegible] ble in water [illegible] water. When [illegible] —19°. It is unsafe to have any [illegible] since it explodes violently [illegible] slightest agitation.

HYPOCHLOROUS ACID HClO

Preparation.—This acid is formed [illegible] by passing [illegible] monoxide into water:

$$Cl_2O + H_2O = 2HClO$$

(2) On agitating chlorine gas with mercuric oxide and water:

$$\begin{array}{ccccccccc} HgO & + & 2Cl_2 & + & H_2O & = & HgCl_2 & + & 2HClO. \\ \text{Mercuric Oxide.} & & \text{Chlorine} & & \text{Water.} & & \text{Mercuric Chloride} & & \text{Hypochlorous Acid} \end{array}$$

The solution is then distilled.

(3) On slowly adding a dilute mineral acid to a clear solution of bleaching powder, in just sufficient amount to decompose the hypochlorite present, hypochlorous acid is formed. A 5 per cent. solution of the acid is recommended as the best for this purpose:

$$\begin{array}{ccccccc} Ca(OCl)_2 & + & 2HNO_3 & = & Ca(NO_3)_2 & + & 2HClO. \\ \text{Calcium Hypochlorite.} & & \text{Nitric Acid.} & & \text{Calcium Nitrate.} & & \text{Hypochlorous Acid.} \end{array}$$

Properties.—The dilute acid is colorless, but when more concentrated it has a yellowish shade. When very dilute it can be distilled without decomposition. The concentrated solution is easily decomposed into chlorine, chloric acid, oxygen, and water. The acid, as well as its salts, possesses a strong oxidizing and bleaching action. Charcoal, iodine, sulphur, phosphorus, arsenic, and antimony are rapidly oxidized when brought in contact with the acid, and, if the latter be concentrated, with explosive violence, forming carbonic, iodic, sulphuric, phosphoric, arsenic, and antimonic acids. Iron filings are immediately oxidized, when brought in contact with the acid, with evolution of chlorine. Copper and mercury under similar circumstances are converted into oxychlorides.

Hypochlorites.—The sodium and calcium salts of this acid are the best known; the former is the important constituent of Labarraque's solution, and the latter of bleaching powder. This bleaching powder, or chlorinated lime, is produced in enormous quantities from the chlorine prepared from the waste hydrochloric acid of the Leblanc soda process, and is used extensively for bleaching and oxidizing, also as a ready and cheap source for chlorine in many smaller operations.

CHLORINE TRIOXIDE, CHLOROUS OXIDE, Cl_2O_3.

Preparation.—(1) Four parts of potassium chlorate and three parts of arsenous oxide are mixed with sufficient water to form a paste; this is then warmed to 60° with a mixture of twelve parts of nitric acid (sp. gr. 1.33) and four parts of water. The reaction is best considered in two stages, as follows:

$$\underset{\substack{\text{Potassium}\\\text{Chlorate.}}}{KClO_3} + \underset{\substack{\text{Arsenous}\\\text{Oxide.}}}{As_2O_3} + \underset{\substack{\text{Nitric}\\\text{Acid.}}}{3HNO_3} = \underset{\substack{\text{Chloric}\\\text{Acid.}}}{HClO_3} + \underset{\substack{\text{Arsenic}\\\text{Oxide}}}{As_2O_5} + \underset{\substack{\text{Nitrogen}\\\text{Trioxide.}}}{N_2O_3} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Potassium}\\\text{Nitrate.}}}{KNO_3}.$$

$$\underset{\substack{\text{Chloric}\\\text{Acid.}}}{2HClO_3} + \underset{\substack{\text{Nitrogen}\\\text{Trioxide}}}{N_2O_3} = \underset{\substack{\text{Chlorine}\\\text{Trioxide.}}}{Cl_2O_3} + \underset{\substack{\text{Nitric}\\\text{Acid.}}}{2HNO_3}.$$

(2) A mixture of arsenous oxide, potassium chlorate, and sulphuric acid which has been diluted with half its volume of water, evolves chlorine trioxide with some violence, according to the following reaction:

$$\underset{\substack{\text{Arsenous}\\\text{Oxide}}}{As_2O_3} + \underset{\substack{\text{Potassium}\\\text{Chlorate}}}{2KClO_3} + \underset{\substack{\text{Sulphuric}\\\text{Acid}}}{2H_2SO_4} + \underset{\text{Water.}}{2H_2O} = \underset{\substack{\text{Acid}\\\text{Potassium}\\\text{Sulphate.}}}{2KHSO_4} + \underset{\substack{\text{Arsenic}\\\text{Acid.}}}{2H_3AsO_4} + \underset{\substack{\text{Chlorine}\\\text{Trioxide}}}{Cl_2O_3}.$$

Some other processes in which certain organic compounds, as sugar or benzene, replace arsenic have been suggested. All methods for the preparation of this compound must be carried out with the greatest care, as a little too much heat may cause dangerous explosions.

Properties.—Chlorine trioxide is a yellowish-green gas with a very irritating odor. This gas is easily condensed to a red-brown liquid, which explodes, on the slightest provocation, with great violence.

CHLOROUS ACID, $HClO_2$.

Preparation.—This acid is formed when chlorine trioxide is passed into water:

$$Cl_2O_3 + H_2O = 2HClO_2.$$

The yellowish solution possesses weak acid properties, is unable to decompose carbonates, but combines with hydrates forming *chlorites*. These salts, as well as the acid itself, are very easily decomposed, especially in the presence of organic matter, and therefore they possess active bleaching properties.

CHLORINE PEROXIDE, Cl_2O_4.

Preparation.—Chlorine peroxide is prepared by adding powdered potassium chlorate to sulphuric acid in a retort, and after solution has taken place gently warming and collecting the heavy gas by displacement:

$$\underset{\substack{\text{Potassium}\\\text{Chlorate.}}}{3KClO_3} + \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{2H_2SO_4} = \underset{\substack{\text{Potassium}\\\text{Perchlorate.}}}{KClO_4} + \underset{\substack{\text{Acid}\\\text{Potassium}\\\text{Sulphate.}}}{2KHSO_4} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Chlorine}\\\text{Peroxide}}}{Cl_2O_4}.$$

With this, as with all other compounds of chlorine and oxygen, great care must be exercised to prevent explosion. When an aqueous solution of the gas is desired, a mixture of potassium chlorate and oxalic acid is heated to 70°, and the mixed chlorine peroxide and carbon dioxide, which are evolved, are passed into water:

$$\underset{\substack{\text{Potassium}\\\text{Chlorate.}}}{2KClO_3} + \underset{\substack{\text{Oxalic}\\\text{Acid.}}}{2H_2C_2O_4} = \underset{\substack{\text{Potassium}\\\text{Oxalate.}}}{K_2C_2O_4} + \underset{\text{Water.}}{2H_2O} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{2CO_2} + \underset{\substack{\text{Chlorine}\\\text{Peroxide.}}}{Cl_2O_4}$$

Properties.—Chlorine peroxide is a heavy, greenish-yellow gas, with a strong, irritating odor. On exposure to a freezing mixture it condenses to a dark-red liquid, which boils at 9° and solidifies at —79°. It is, perhaps, the most dangerous of all the oxides of chlorine, as it readily decomposes, forming one volume of chlorine and two volumes of oxygen. Many organic substances, when brought in contact with the gas, are inflamed. When dissolved in water it forms a yellow solution, which does not appear to have acid properties, since on adding an alkali to the solution a mixture of chlorite and chlorate is formed.

CHLORIC ACID, $HClO_3$.

This acid is only known in solution and in combination with certain bases as chlorates.

Preparation.—Barium chlorate is decomposed by the equivalent quantity of diluted sulphuric acid:

$$\underset{\substack{\text{Barium}\\\text{Chlorate.}}}{Ba(ClO_3)_2} + \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{H_2SO_4} = \underset{\substack{\text{Barium}\\\text{Sulphate.}}}{BaSO_4} + \underset{\substack{\text{Chloric}\\\text{Acid.}}}{2HClO_3}$$

The clear liquid is decanted from the precipitated barium sulphate and evaporated in a vacuum over sulphuric acid. The most concentrated solution obtainable by this method contains 40 per cent of water. On further concentration it decomposes into perchloric acid, chlorine, and oxygen, according to the following:

$$\underset{\substack{\text{Chloric}\\\text{Acid.}}}{8HClO_3} = \underset{\substack{\text{Perchloric}\\\text{Acid.}}}{2HClO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Oxygen.}}{3O_2} + \underset{\text{Chlorine.}}{2Cl_2}$$

Chloric acid can also be prepared by adding to potassium chlorate solution a slight excess of hydrofluosilicic acid:

$$\underset{\substack{\text{Potassium}\\\text{Chlorate.}}}{2KClO_3} + \underset{\substack{\text{Hydrofluosilicic}\\\text{Acid.}}}{H_2SiF_6} = \underset{\substack{\text{Potassium}\\\text{Silicofluoride.}}}{K_2SiF_6} + \underset{\substack{\text{Chloric}\\\text{Acid.}}}{2HClO_3}$$

The clear liquid is decanted from the insoluble potassium silicofluoride, [illegible] is added and the solution evap rated, when the excess of hydrofluosilicic acid, combining with the added silica, passes off as silicon tetrafluoride, and the excess of silica settles. The solution of chloric acid may now be decanted pure. The acid containing 40 per cent. of water corresponds to the formula $HClO_3.7H_2O$.

Properties.—When of the above strength, chloric acid is a syrupy liquid, almost colorless, and of a faint chlorous odor. It has a powerful acid reaction, and in other chemical properties resembles nitric acid. It decomposes organic matter with evolution of heat and light. Sulphur and phosphorus are inflamed on coming in contact with it.

Chlorates.—Chloric acid is monobasic, and its salts are called chlorates. The potassium and sodium salts are official under the titles **Potassii Chloras** and **Sodii Chloras**. The chlorates are all soluble in water. Potassium chlorate, which is soluble in 16.5 parts of water, is one of the most insoluble of the potassium salts, while sodium chlorate requires only 1.1 parts of water to effect solution. When a hot concentrated solution of a hydrate is saturated with chlorine the result is a chloride and a chlorate, as follows:

$$\underset{\substack{\text{Potassium}\\\text{Hydrate.}}}{6KOH} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\substack{\text{Potassium}\\\text{Chloride.}}}{5KCl} + \underset{\substack{\text{Potassium}\\\text{Chlorate.}}}{KClO_3} + \underset{\text{Water.}}{3H_2O.}$$

When, however, a cold dilute solution of the alkali is used, a hypochlorite is formed instead of a chlorate, according to the following reaction:

$$\underset{\substack{\text{Potassium}\\\text{Hydrate.}}}{2KOH} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\substack{\text{Potassium}\\\text{Chloride.}}}{KCl} + \underset{\substack{\text{Potassium}\\\text{Hypochlorite.}}}{KClO} + \underset{\text{Water.}}{H_2O.}$$

On the commercial scale potassium chlorate is prepared by passing chlorine into boiling milk of lime, and to this is added the proper proportion of potassium chloride, when double decomposition takes place with formation of calcium chloride and potassium chlorate. Calcium chloride is very soluble, while the less soluble potassium chlorate crystallizes out:

$$\underset{\substack{\text{Calcium}\\\text{Hydrate.}}}{6Ca(OH)_2} + \underset{\text{Chlorine.}}{6Cl_2} = \underset{\substack{\text{Calcium}\\\text{Chloride.}}}{5CaCl_2} + \underset{\substack{\text{Calcium}\\\text{Chlorate.}}}{Ca(ClO_3)_2} + \underset{\text{Water.}}{6H_2O.}$$

$$\underset{\substack{\text{Calcium}\\\text{Chlorate.}}}{Ca(ClO_3)_2} + \underset{\substack{\text{Potassium}\\\text{Chloride.}}}{2KCl} = \underset{\substack{\text{Calcium}\\\text{Chloride.}}}{CaCl_2} + \underset{\substack{\text{Potassium}\\\text{Chlorate.}}}{2KClO_3.}$$

A recent improvement substitutes magnesium oxide or hydrate for lime, and, after concentrating the solution of mixed chlorate and chloride to 72° Tw., reducing the temperature to —17°. The refrigeration causes the separation of one-seventh more chlorate, and the magnesium chloride is available to be used as such, or reconverted into hydrate to be used again. The chlorates are also made now by electrolyzing potassium or sodium chlorides and allowing the nascent oxygen to act upon the hypochlorites first produced. In this case the electrolyzing cell must be separated by a porous partition into a positive and a negative compartment, in the latter of which the chlorates form.

The chlorates melt on the application of heat, and then give off oxygen. When melted they energetically decompose such organic substances as are brought in contact with them. The dry chlorate should not be triturated with organic matter or sulphur. Such dry mixtures explode violently by percussion or rubbing, and burn brilliantly on the application of flame.

Impurities and Tests.—Chlorides, when present, are detected by giving a white precipitate with silver nitrate, soluble in ammonium hydrate and insoluble in nitric acid. Nitrates may be detected by heating the solution with zinc and potassium hydrate; in the presence of this impurity ammonia will be formed, which will turn red litmus paper blue and furnish the other evidences of its presence.

Uses.—In addition to their use in medicine, the chlorates are largely employed as an oxidizing agent in dyeing and calico-printing and in the manufacture of colored fires. In the preparation of these fireworks potassium chlorate and some organic substance, as sugar, starch, shellac, or wheat bran, are separately pulverized and then intimately mixed, avoiding friction or anything that might cause ignition or explosion. To this mixture is then added pulverized barium nitrate for green, strontium nitrate for red, sodium nitrate for yellow, and copper oxide for blue. Sulphur is sometimes an ingredient of these mixtures, but it greatly increases the risk of spontaneous combustion or explosion.

PERCHLORIC ACID, $HClO_4$.

Preparation.—Perchloric acid is produced in the decomposition of chloric acid, but this is not used as a method of preparing it. The process consists in first preparing potassium perchlorate by heating the chlorate. The latter salt, when heated to 350°, gives off a part of its oxygen and becomes a past mass of perchlorate and chloride.

$$2KClO_3 = KClO_4 + KCl + O_2.$$

The pasty mass is cooled, powdered, and treated with cold water to remove the potassium chloride. The undissolved residue is then digested with warm hydrochloric acid to decompose any chlorate and convert it into chloride, which is then washed out with cold water. The residue which now remains consists of nearly pure perchlorate. On heating the perchlorate in a retort with four times its weight of concentrated sulphuric acid to 110°, pure perchloric acid distils over. If the distillation be long continued, partial decomposition of the salt occurs, some water is formed, which, distilling over with the acid, causes the distillate to solidify in a crystalline mass, consisting of a hydrate with the formula $HClO_4.H_2O$. On redistilling this solid compound the pure acid first passes over at 203°, and a compound having the composition $HClO_4.2H_2O$ remains behind. This second distillation is necessary in order to get a pure acid, since in the decomposition of the first some of the sulphuric acid is liable to be carried over mechanically.

Properties.—Perchloric acid is a colorless volatile liquid, which fumes strongly on coming in contact with moist air. Its specific gravity is 1.782 at 15.5°. It dissolves in water with a hissing noise, and, when brought in contact with organic matter, causes the latter to ignite. The concentrated acid, on standing, even in the dark, rapidly decomposes, becoming dark yellow to brown in color, and finally explodes with violence. By carefully adding water until crystals form, it is converted into the hydrate, $HClO_4.H_2O$. These crystals melt at 50°, and are strongly oxidizing in their action. The diluted acid has a pure sour taste, and reddens litmus paper without bleaching it. Iron and zinc dissolve in the diluted acid, causing evolution of hydrogen.

Perchlorates.—These are nearly all quite soluble in water, and some of them are deliquescent. The potassium salt is one of the most insoluble, requiring fifty-eight parts of water to dissolve it.

Perchlorates are distinguished from the chlorates by decomposing into chlorides at a higher temperature, by remaining undecomposed on the addition of hydrochloric acid, and by not yielding ClO_2 on the addition of concentrated sulphuric acid. From chlorides they are distinguished by giving no precipitate with silver nitrate, and from both nitrates and chlorates by not decolorizing indigo solution on the addition of hydrochloric acid.

OXYGEN AND BROMINE.

Unlike chlorine, bromine appears to form no stable oxygen; the following acids, however, show a simil oxygen compounds of these two halogen elements:

Hypobromous acid,	$HBrO$.
Bromic acid,	$HBrO_3$.
Perbromic acid,	$HBrO_4$.

HYPOBROMOUS ACID, HBrO.

Preparation.—This compound is prepared by agitating mercuric oxide, water, and bromine, when the following place:

$$\underset{\text{Mercuric Oxide.}}{2HgO} + \underset{\text{Bromine.}}{2Br_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Hypobromous Acid.}}{2HBrO} + \underset{\text{M Oxy}}{Hg}$$

By successive additions of bromine and mercuric oxide, a be obtained containing 6.2 per cent. of the acid. This so poses under ordinary circumstances on heating, but in a v be distilled unchanged at 40°.

Properties.—The aqueous acid has a yellow color, and oxidizing and bleaching agent.

The calcium salt of hypobromous acid has been prepar bromine to calcium hydrate. Very little, however, is known that it resembles the corresponding salt of chlorine in its act

BROMIC ACID, HBrO₃.

Preparation.—Bromic acid is prepared by first obtaining from bromine and a hydrate:

$$\underset{\text{Bromine.}}{3Br_2} + \underset{\text{Potassium Hydrate.}}{6KOH} = \underset{\text{Potassium Bromide.}}{5KBr} + \underset{\text{Potassium Bromate.}}{KBrO_3} + \underset{\text{Wa}}{3H}$$

The bromate being less soluble than the bromide is easil from it by crystallization.

The bromate is then decomposed by acid. As most pot are soluble, it is preferable to take a base which forms an ins pound with some mineral acid; for this purpose silver and bariu have been recommended. The latter salt is cheap and easily d by sulphuric acid, as follows:

$$\underset{\text{Barium Bromate.}}{Ba(BrO_3)_2} + \underset{\text{Sulphuric Acid.}}{H_2SO_4} = \underset{\text{Barium Sulphate.}}{BaSO_4} + \underset{\text{Bromic Acid.}}{2HBrO}$$

It requires some care to add the exact amount of sulphuric sary to precipitate all the barium, and when this is accomplish solution is decanted from the insoluble barium sulphate.

Properties.—The nearly colorless acid solution cannot be co by heat, since it decomposes at 100° into bromine and oxyg evaporating at ordinary temperatures in a vacuum over sulphu may be reduced to a strength corresponding to the formula $HBrO_3.7H_2O$. Further concentration even at ordinary temperatures causes decomposition. In many of its properties it closely resembles chloric acid.

The bromates are generally soluble in water, and are decomposed on heating. Some give off oxygen with formation of bromides, while others evolve both bromine and oxygen, leaving an oxide of the metal.

Perbromic acid, $HBrO_4$, is said to have been discovered, but subsequent investigators have failed to confirm this.

OXYGEN AND IODINE.

One oxide and two acids of these elements are known, as follows:

Oxide.	Acids.
Iodine pentoxide, I_2O_5.	Iodic acid, HIO_3.
	Periodic acid, HIO_4.

IODINE PENTOXIDE, I_2O_5.

Preparation.—One part of iodine is heated with ten parts of pure concentrated nitric acid until complete solution takes place and there are no more fumes evolved. On evaporating until a temperature of 200° is attained, all the nitric acid is removed and a white residue remains. The reaction may be best expressed in two stages, as follows:

$$\underset{\text{Iodine.}}{3I_2} + \underset{\text{Nitric Acid.}}{10HNO_3} = \underset{\substack{\text{Iodic}\\\text{Acid.}}}{6HIO_3} + \underset{\substack{\text{Nitrogen}\\\text{Dioxide.}}}{5N_2O_2} + \underset{\text{Water.}}{2H_2O}.$$

$$\underset{\substack{\text{Iodic}\\\text{Acid.}}}{6HIO_3} = \underset{\substack{\text{Iodine}\\\text{Pentoxide.}}}{3I_2O_5} + \underset{\text{Water.}}{3H_2O}.$$

Properties.—Iodine pentoxide is a white, crystalline powder, having a specific gravity of 4.487. On heating to 300° it is decomposed into iodine and oxygen. It is very soluble in water, and, when dissolved in an amount to form a syrupy liquid, the solution on standing deposits crystals of iodic acid.

IODIC ACID, HIO_3.

Preparation.—The simplest method of preparation is by dissolving the above oxide in water:

$$I_2O_5 + H_2O = 2HIO_3.$$

It may also be prepared from barium iodate and sulphuric acid. The iodate is made by dissolving powdered iodine in hot concentrated solution of potassium chlorate, and adding a few drops of nitric acid. After the evolution of chlorine has ceased and the solution has become cool, crystals of potassium iodate separate out. On dissolving this salt in water and adding barium chloride, barium iodate separates out as a white solid. This is then decomposed by the careful addition of sulphuric acid. The three reactions take place as follows:

$2KClO_3$	$+$	I_2	$=$	$2KIO_3$	$+$	Cl_2.
Potassium Chlorate.		Iodine.		Potassium Iodate.		Chlorine.

$2KIO_3$	$+$	$BaCl_2$	$=$	$Ba(IO_3)_2$	$+$	$2KCl$.
Potassium Iodate.		Barium Chloride.		Barium Iodate.		Potassium Chloride.

$Ba(IO_3)_2$	$+$	H_2SO_4	$=$	$BaSO_4$	$+$	$2HIO_3$.
Barium Iodate.		Sulphuric Acid.		Barium Sulphate.		Iodic Acid.

Iodic acid is also formed when chlorine is passed into water in which finely-powdered iodine is suspended:

I_2	$+$	$5Cl_2$	$+$	$6H_2O$	$=$	$2HIO_3$	$+$	$10HCl$.
Iodine.		Chlorine.		Water.		Iodic Acid.		Hydrochloric Acid.

The hydrochloric acid is removed by moist, freshly-precipitated silver oxide.

Properties.—Iodic acid occurs in the form of colorless, rhombic crystals, having a specific gravity of 4.629 at 0°. It is very soluble in water, but insoluble in alcohol. On heating to 170° the acid decomposes into iodine pentoxide and water. Organic matter, phosphorus, and sulphur inflame on coming into contact with the acid. Sulphurous oxide, sulphuretted hydrogen, and hydriodic acid decompose it with liberation of iodine:

$2HIO_3$	$+$	$5SO_2$	$+$	$4H_2O$	$=$	I_2	$+$	$5H_2SO_4$.
Iodic Acid.		Sulphur Dioxide.		Water.		Iodine.		Sulphuric Acid.
$2HIO_3$	$+$	$5H_2S$	$=$	I_2	$+$	$5S$	$+$	$6H_2O$.
Iodic Acid.		Hydrogen Sulphide.		Iodine.		Sulphur.		Water.
HIO_3	$+$	$5HI$	$=$	$3I_2$	$+$	$3H_2O$.		
Iodic Acid.		Hydriodic Acid.		Iodine.		Water.		

The iodates are mostly soluble in water. On heating, some of them decompose into oxygen and an iodide, while others give off both oxygen and iodine, a metallic oxide remaining. The iodates are detected by adding to the solution a small quantity of sulphurous acid or a sulphate, to liberate iodine, and then a dilute solution of starch, with which the latter forms a blue color.

PERIODIC ACID, HIO_4.

Preparation.—This acid is only known in the free state with two molecules of water. It is obtained most readily by acting on perchloric acid with iodine:

$2HClO_4$	$+$	I_2	$+$	$2H_2O$	$=$	$2HIO_4.2H_2O$	$+$	Cl_2.
Perchloric Acid.		Iodine.		Water.		Periodic Acid.		Chlorine.

Properties.—This compound consists of colorless, transparent crystals, which are deliquescent and readily soluble in water. They melt at 133° to 140°, and on the further increase of heat are decomposed into iodine pentoxide, water, and oxygen.

SULPHUR.

Symbol, S. *Atomic Weight*, 31.98. *Valence*, II.

Sulphur was known to the ancients.

Occurrence.—It occurs in the free state, mixed with earthy matter, in the vicinity of extinct as well as active volcanoes. Its existence in the free state is supposed to be due to the sulphur dioxide and hydrogen sulphide in volcanic gases, which, reacting on each other, form sulphur, as follows:

$$SO_2 + 2H_2S = 2H_2O + S_3.$$

In combination sulphur is found, as sulphide, combined with iron, lead, zinc, copper, mercury, and some other metals in smaller amount; as sulphate, combined with calcium in gypsum, with barium in heavy spar, with magnesium in kieserite, and with sodium and potassium. Sulphur also exists in the vegetable and animal kingdoms, combined in various organic compounds, and in some mineral waters as hydrogen sulphide.

Source.—The principal source of sulphur has always been the volcanic districts in the island of Sicily and the other volcanic regions that border the Mediterranean.

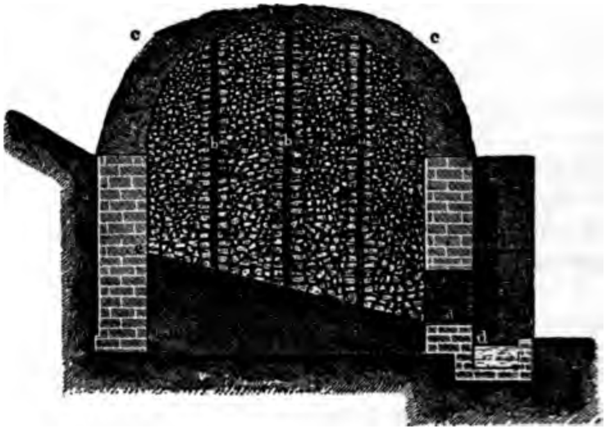
In recent years very large deposits have been found in the United States. A large mine is worked near Santa Barbara, in California. Two hundred miles south of Salt Lake City, at Cove Springs, Utah, a deposit of sulphur exists two thousand feet square and of unknown depth; shafts have been sunk to the depth of sixty feet without reaching the bottom. This sulphur is free from antimony and arsenic. The annual output in Utah and Nevada amounts to several thousand tons. The cost of transportation is the greatest obstacle to our obtaining all our sulphur from these sources. The exportation from Sicily amounts to about 200,000 tons annually. In 1892 the United States consumed 100,721 tons of Sicilian sulphur and 1825 tons of the American product. In addition to this, there were used 210,000 tons of imported pyrites, containing 43 per cent. of sulphur, and 119,000 tons of American pyrites, containing 44 per cent. of sulphur.

In addition to the above sources, sulphur is found in Iceland, Mexico, Central America, and the Sandwich Islands. Volcanoes in all these places either are or have been the cause of the deposit. In Mexico the sulphur is hoisted in buckets from the crater of Popocatapetl.

Extraction and Purification.—The sulphur earth and masses of ore are piled, with a small amount of fuel, in heaps over depressions in the earth. The heaps are then ignited; the sulphur melts, runs down, and is collected from the hollow beneath.

Only about one-third of the sulphur is saved by this means, the other two-thirds being consumed in heating. This process has been modified from time to time, so as to decrease the loss. One of these modifications, shown in Fig 51, consists of a furnace of mason-work, with an inclined bottom. When the ore is filled in, a number of channels are left to assist in the distribution of the heat, and over the top of all is placed a layer of powdered ore and then a layer of the burnt ore. The pile is then ignited at the bottom of the furnace, and the sulphur running down the inclined bottom is removed at the mouth. The principal advantages of this process arise from the increased size of the furnace and the closed bottom, which enables one to control the operation, so that less sulphur is burned. Some of these furnaces are as much as 10 meters in diameter, and several weeks are required to complete one charge. The richest ores, containing 30 to 40 per cent. of sulphur, yield as much as 25 per cent., and the poorer ones, containing 20 to 25 per cent., yield 10 to 15 per cent.

FIG. 51.



Extraction of sulphur..

More recently a method has been introduced in which the ore is placed in a perforated basket and then immersed in solution of calcium chloride of such strength that its boiling point is higher than that at which sulphur melts, 114.5°. Under these conditions the sulphur melts out from its ore, and sinks to the bottom of the tank, where it is drawn off in a comparatively pure form.

The alkali waste in the Leblanc soda process consists of calcium sulphide. This product, before removal from the leaching vats, is subjected to a current of air by which the sulphide is partly converted into sulphite and thiosulphate. The mixture is then treated with hydrochloric acid, when the following reaction takes place:

$$\underset{\substack{\text{Calcium}\\\text{Sulphide.}}}{2CaS} + \underset{\substack{\text{Calcium}\\\text{Thiosulphate.}}}{CaS_2O_3} + \underset{\substack{\text{Hydrochloric}\\\text{Acid.}}}{6HCl} = \underset{\substack{\text{Calcium}\\\text{Chloride.}}}{3CaCl_2} + \underset{\text{Sulphur.}}{4S} + \underset{\text{Water.}}{3H_2O.}$$

A newer and as it seems more satisfactory process is that of Chance. The alkali waste is first decomposed according to the reactions:

$$2CaS + CO_2 + H_2O = CaCO_3 + Ca(SH)_2 \text{ and}$$

$$Ca(SH)_2 + CO_2 + H_2O = CaCO_3 + 2H_2S.$$

The hydrogen sulphide gas, mixed with air, is then passed over oxide of iron at a low red heat, when the hydrogen burns with separation of sulphur:

$$H_2S + O = H_2O + S.$$

In England the sulphur is recovered from the purifiers in the gas-works. The gas, which contains hydrogen sulphide, is passed over moist ferric hydrate, when the following reaction takes place:

$$\underset{\substack{\text{Ferric}\\\text{Hydrate.}}}{Fe_2(OH)_6} + \underset{\substack{\text{Hydrogen}\\\text{Sulphide.}}}{3H_2S} = \underset{\substack{\text{Ferrous}\\\text{Sulphide.}}}{2FeS} + \underset{\text{Sulphur.}}{S} + \underset{\text{Water.}}{6H_2O.}$$

The mass is then exposed to the air, by which sulphur is deposited, and the hydrate regenerated, as follows:

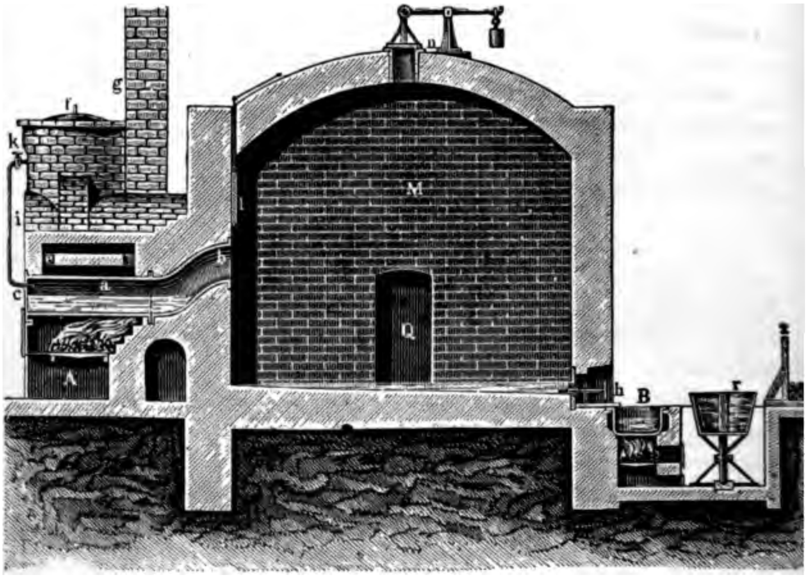
$$\underset{\substack{\text{Ferrous}\\\text{Sulphide.}}}{2FeS} + \underset{\text{Water.}}{3H_2O} + \underset{\text{Oxygen.}}{3O} = \underset{\substack{\text{Ferric}\\\text{Hydrate.}}}{Fe_2(OH)_6} + \underset{\text{Sulphur.}}{S_2.}$$

The hydrate, mixed with sulphur, is then exposed to another quantity of the gas, and again regenerated until the mass contains 50 per cent. of sulphur; the latter is then recovered by heating the mixture.

In France, Germany, and Sweden, sulphur is largely obtained by distilling iron pyrites; such sulphur is liable to contain considerable quantities of arsenic.

The crude sulphur, as obtained by the various processes just described, contains 2 or 3 per cent. of impurities. To remove these the process of sublimation is resorted to. A furnace similar to that in Fig. 52 is employed. The crude sulphur is melted in the vessel K, with the waste heat from the furnace; it is then run in small quantities at a time into the retort *a*, from which it sublimes into the large chamber M. At first, while the chamber is cool, the sulphur is deposited in fine powder, but as the whole becomes heated it melts and is run off at the bottom into moulds, and becomes the roll sulphur or brimstone of commerce.

FIG. 52.



Sublimation of sulphur.

Properties.—Sulphur is a lemon-yellow, crystalline solid, odorless, and almost without taste. It is insoluble in water, almost insoluble in alcohol, ether, and volatile oils, but easily soluble in fixed oils. Its specific gravity at 0° is 2.05. On the application of heat sulphur melts at 114.5°, and remains liquid until cooled to 111°. The liquid is straw-yellow at first, but becomes dark red and viscid on gradually raising the temperature from 200° to 250°, when it is too thick to pour, and becom almost black in color. A further increase of temperature caus the sulphur to become thin in consistence, but it remains dark in color, and at 448.4° it boils under ordinary pressure.

Sulphur, as above described, exists in the form of rhombic octahedra, that being the form in which it occurs in nature, as well as that in which it forms from solution in carbon disulphide. When, however, certain conditions are complied with, sulphur may easily be obtained in several allotropic modifications. On heating it in a Hessian crucible until melted, allowing to cool until a crust forms on the surface, and then quickly pouring out the liquid portion, the crucible will be lined with long, brilliant, transparent crystals, having the form of monoclinic prisms; these become opaque after twenty-four hours at ordinary temperature, and are then found to be made up of minute rhombic crystals. Monoclinic sulphur has a specific gravity of 1.96, melts at 120°, and is soluble in carbon disulphide.

Another modification may be prepared by carefully heating sulphur to 330°, and then pouring in a thin stream into water. The product in this case is an amber-colored, elastic mass, which may be drawn out into threads or kneaded between the fingers. This is called the plastic variety. It has a specific gravity of 1.957, and is insoluble in carbon disulphide. At 100° it quickly reverts to the rhombic variety with evolution of heat, hence no melting point can be assigned to it.

An insoluble variety similar to this is formed when hydrochloric acid is added to calcium pentasulphide. Small quantities of this insoluble variety are also frequently found in sublimed sulphur.

On heating sulphur in the air to about 230° it inflames, combining with the oxygen of the air to form sulphur dioxide. In the presence of air and moisture the finely-divided sulphur is slowly oxidized at ordinary temperatures, forming sulphurous and sulphuric acids.

Sulphur combines directly with many other non-metals, as hydrogen, chlorine, bromine, iodine, and phosphorus, and with most metals.

SULPHUR AND HYDROGEN.

HYDROGEN SULPHIDE.

SULPHURETTED HYDROGEN.

Formula, H_2S. *Molecular Weight*, 33.98.

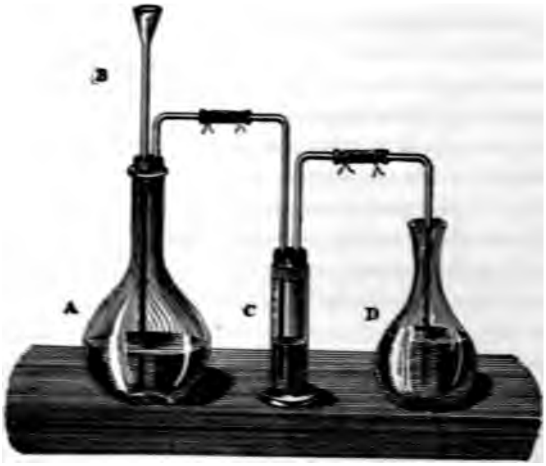
History.—Hydrogen sulphide was noticed by the ancients, but Scheele, in 1777, was the first to investigate it by heating sulphur with hydrogen.

Occurrence.—It occurs in nature when organic bodies containing sulphur putrefy, in volcanic gases, and in many mineral waters. The sulphur waters in Virginia are the most important in the United States.

Preparation.—Hydrogen sulphide is formed when a stream of hydrogen is passed over sulphur heated to the boiling point.

For all practical purposes, however, an apparatus similar to that illustrated in Fig. 53 answers the purpose most satisfactorily.

FIG. 53.



Preparation of hydrogen sulphide.

In the generator, A, is placed some ferrous sulphide, and to it [illegible] added sulphuric acid, previously diluted with six volumes of water, when the following reaction takes place.

$$\underset{\text{Ferrous Sulphide.}}{FeS} + \underset{\text{Sulphuric Acid.}}{H_2SO_4} = \underset{\text{Ferrous Sulphate.}}{FeSO_4} + \underset{\text{Hydrogen Sulphide.}}{H_2S.}$$

The gas is readily evolved without the application of heat, and may either be used directly or passed through a little water in the wash-bottle at C. When it is desired to prepare the solution of the gas it is passed into water in the flask D.

Ferrous sulphide frequently contains metallic iron, in which case the gas will contain some free hydrogen. This is rarely an objection, but, if it should be, then a pure gas may be obtained by treating antimonous sulphide with hydrochloric acid:

Sb_2S_3	+	$6HCl$	=	$2SbCl_3$	+	$3H_2S.$
Antimonous Sulphide.		Hydrochloric Acid.		Antimonous Chloride.		Hydrogen Sulphide.

The gas may also be prepared by heating in a flask a mixture of paraffin and sulphur; a number of other organic substances may be used in place of the paraffin.

Properties.—Hydrogen sulphide is a colorless gas with a disagreeable odor and a sweetish taste. Its density is 16.99. One volume of water dissolves 4.37 volumes of the gas at 0°, and 3.23 volumes at 15°.

The solution reddens litmus, and rapidly undergoes change on exposure to air, water and sulphur being the result, the latter separating out. Under a pressure of 17 atmospheres the gas condenses to a liquid, which solidifies at $-85°$. Liquefaction may also be accomplished under the ordinary atmospheric pressure by passing the gas through a tube cooled to $-70°$.

Hydrogen sulphide is a very inflammable gas, burning with a pale-blue flame. The products of its combustion are water, sulphur dioxide, and sulphur, which is deposited. The gas is decomposed by many oxidizing agents; chlorine, for example, changes it immediately, according to the following reaction:

$$H_2S + Cl_2 = 2HCl + S.$$

A similar reaction takes place with bromine and with iodine; in the latter case, however, the reaction is only possible in the presence of water. This is explained by the fact that the reaction is attended by an absorption of heat, and unless something is present to supply this loss the change will not take place. When hydrogen iodide is absorbed by water heat is evolved and makes up for the loss occasioned by the first part of the operation.

Hydrogen sulphide combines with many metals, decomposing their oxides, hydrates, or carbonates. Many of the metallic sulphides possess characteristic colors. This fact adds to the value of the gas or its solution in chemical analysis.

The solution has also been used medicinally; it is given internally in about one-half ounce doses.

The Sulphides.—Many of these compounds occur native, and after a proper purification are ready for use. When, however, it is desired to prepare a sulphide, it is usually accomplished by heating together sulphur and the metal, or by passing hydrogen sulphide into a solution of the metallic chloride. In some cases an alkali is necessary in order to neutralize the free acid formed; in other cases the precipitation takes place best in hydrochloric acid solution.

HYDROGEN PERSULPHIDE, H_2S_2.

This compound, which is the counterpart of hydrogen dioxide, exists in the form of a yellow oily liquid. It is prepared by boiling together 1 part of slaked lime, 6 parts of water, and 2 parts of sublimed sulphur, and pouring the clear solution into cold concentrated hydrochloric acid. The heavy, yellowish, oily compound separates and sinks to the bottom. It possesses an odor similar to that of hydrogen sulphide, and an acrid, unpleasant taste. It readily decomposes into hydrogen sulphide and sulphur. The most interesting feature of this compound is its combination with strychnine, forming a beautiful compound, having the formula $2C_{21}H_{22}N_2O_2 + 3H_2S_2$.

SULPHUR AND CHLORINE.

These elements combine directly to form three distinct compounds.

Sulphur Monochloride, S_2Cl_2, is formed by passing dry chlorine over dry sulphur. A reddish-yellow liquid is formed, which may be rectified by distillation. It has a specific gravity of 1.705, and boils at 138°. It is a solvent of sulphur to the extent of 66 per cent., forming a thick syrupy liquid which is used in vulcanizing rubber.

Sulphur Dichloride, SCl_2, is formed when dry chlorine is passed into the monochloride at 0°. The excess of chlorine is removed by passing carbon dioxide through the liquid. The dichloride is an unstable, dark-red liquid, slowly decomposing at ordinary temperatures into the monochloride and chlorine. The same decomposition takes place on the addition of water.

Sulphur Tetrachloride, SCl_4, is prepared by passing chlorine into the dichloride at a temperature of —20° to —22°. This is a mobile, yellowish-brown liquid, which decomposes as the temperature rises from —20°. On the addition of water the decomposition takes place with explosive rapidity.

SULPHUR AND BROMINE.

Bromine Monosulphide, S_2Br_2, is the only compound of these two elements known at the present time. It is prepared by the direct union of the elements, the excess of bromine being removed by carbon dioxide. It is a heavy, red liquid, which is stable at ordinary temperatures, but decomposes slowly at the boiling point, 200° to 210°, into sulphur and bromine.

SULPHUR AND IODINE.

These two elements unite in two proportions.

Sulphur Moniodide, S_2I_2, is formed when the two elements are heated together under water, or, according to the Pharmacopœia, without water in a loosely-stoppered flask. They are directed to be first thoroughly mixed and then gently heated until the mass becomes of a uniform, dark color, when the temperature is increased to the point necessary to melt them. After cooling, the grayish-black mass is rubbed to powder. Thus prepared **Sulphuris Iodidum**, U. S. P., is a grayish-black, crystalline solid, with the characteristic odor of iodine, having a somewhat acrid taste and a slightly acid reaction. It is insoluble in water, soluble in sixty parts of glycerin, and very soluble in carbon disulphide. Alcohol and ether remove the iodine, leaving the sulphur. It is gradually decomposed on exposure to the air with loss of iodine. On the application of heat it melts at 60°, and at a higher temperature sublimes with partial decomposition, without leaving any residue. Prolonged boiling with water removes the iodine, which escapes with the steam, leaving the sulphur.

Sulphur Hexiodide, SI_6, is obtained by evaporating a solution of the two elements in carbon disulphide, when crystals similar to those of iodine separate.

SULPHUR AND OXYGEN.

The following compounds of these two elements are known:

Sulphur sesquioxide,	S_2O_3.
Sulphur dioxide,	SO_2.
Sulphur trioxide,	SO_3.
Sulphur heptoxide,	S_2O_7.

Two of these, S_2O_3 and S_2O_7, are of interest only as chemical compounds, while the others, SO_2 and SO_3, are well known both in medicine and in the arts. They form, by uniting with water, two well-known acids, as follows:

$SO_2 + H_2O = H_2SO_3$, Sulphurous acid.
$SO_3 + H_2O = H_2SO_4$, Sulphuric acid.

There are also the following acids, the oxides corresponding to which have not been discovered:

H_2SO_2,	Hyposulphurous acid.
$H_2S_2O_3$,	Thiosulphuric acid.
$H_2S_2O_6$,	Dithionic acid.
$H_2S_3O_6$,	Trithionic acid.
$H_2S_4O_6$,	Tetrathionic acid.
$H_2S_5O_6$,	Pentathionic acid.

SULPHUR SESQUIOXIDE, S_2O_3.

This compound is formed when sulphur is added, in small quantity at a time, to sulphur trioxide. It separates as a dark-blue liquid, which solidifies into bluish-green, crystalline crusts:

$$SO_3 + S = S_2O_3.$$

It readily decomposes into sulphur dioxide and sulphur:

$$2S_2O_3 = 3SO_2 + S.$$

HYPOSULPHUROUS ACID, H_2SO_2.

This compound was called hydrosulphurous acid by Schützenberger, its discoverer. The above title, however, is more in accordance with its constitution. It should not be confounded with *thiosulphuric acid*, which is sometimes improperly called hyposulphurous acid.

Preparation.—When zinc is added to sulphurous acid the following reaction takes place:

$$\underset{\text{Zinc.}}{Zn} + \underset{\substack{\text{Sulphurous}\\\text{Acid.}}}{H_2SO_3} = \underset{\substack{\text{Zinc}\\\text{Sulphite.}}}{ZnSO_3} + \underset{\text{Hydrogen.}}{H_2}.$$

$$\underset{\substack{\text{Sulphurous}\\\text{Acid.}}}{H_2SO_3} + \underset{\text{Hydrogen}}{H_2} = \underset{\substack{\text{Hyposulphurous}\\\text{Acid.}}}{H_2SO_2} + \underset{\text{Water.}}{H_2O}.$$

Properties.—This is a yellow liquid with powerful reducing properties. On exposure to air it is rapidly decomposed, as follows:

$$\underset{\substack{\text{Hyposulphurous}\\\text{Acid}}}{2H_2SO_2} = \underset{\substack{\text{Sulphur}\\\text{Dioxide.}}}{SO_2} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Sulphur.}}{S}.$$

It is a more powerful bleaching agent than sulphurous acid, and precipitates a number of the metals from solutions of their salts, for example:

$$\underset{\substack{\text{Mercuric}\\\text{Chloride.}}}{HgCl_2} + \underset{\substack{\text{Hyposulphurous}\\\text{Acid.}}}{H_2SO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Mercury.}}{Hg} + \underset{\substack{\text{Hydrochloric}\\\text{Acid.}}}{2HCl} + \underset{\substack{\text{Sulphurous}\\\text{Acid.}}}{H_2SO_3}.$$

This serves to distinguish it from sulphurous acid. Salts of this acid have been formed, which are true hyposulphites. When sodium bisulphite is treated with zinc, the mixture kept cool, and air excluded, the hyposulphite is formed according to the following reaction:

$$\underset{\substack{\text{Sodium}\\\text{Bisulphite}}}{3NaHSO_3} + \underset{\text{Zinc.}}{Zn} = \underset{\substack{\text{Acid Sodium}\\\text{Hyposulphite.}}}{NaHSO_2} + \underset{\substack{\text{Sodium}\\\text{Sulphite.}}}{Na_2SO_3} + \underset{\substack{\text{Zinc}\\\text{Sulphite.}}}{ZnSO_3} + \underset{\text{Water.}}{H_2O}.$$

The zinc and sodium sulphites crystallize out as a double salt, the solution is mixed with four times its volume of strong alcohol, by which the remainder of this salt is removed, and the solution is set aside, when crystals of the hyposulphite separate. These should be dried in a vacuum.

SULPHUR DIOXIDE

Formula, SO_2. *Molecular Weight*, 63.90.

History.—Sulphur dioxide, or sulphurous oxide, was readily recognized by the ancients, since it is always formed when sulphur is burned in the air.

Occurrence.—It occurs native as a volcanic gas, and is foun in small quantity in the air of large cities, on account of th existence of sulphur in coal.

Preparation.—(1) When sulphur is burned in air or oxyge direct union of the elements takes place with the formation of sulphur dioxide:

$$S_2 + 2O_2 = 2SO_2.$$

This process of burning is used for nearly all cases where the gas is made on a large scale, as in bleaching and the manufacture of sulphites and sulphuric acid.

(2) When three parts of sulphur are mixed with four parts of manganese dioxide, and the mixture is heated, sulphur dioxide is given off:

$$\underset{\text{Sulphur.}}{S_2} + \underset{\substack{\text{Manganese}\\\text{Dioxide.}}}{MnO_2} = \underset{\substack{\text{Manganous}\\\text{Sulphide.}}}{MnS} + \underset{\substack{\text{Sulphur}\\\text{Dioxide.}}}{SO_2.}$$

(3) On a smaller scale for laboratory purposes, copper turnings in a glass flask are covered with strong sulphuric acid and the mixture heated gradually, so as to maintain a steady effervescence. Mercury and silver give the same result. Some sulphide is formed at the same time, but the reaction is practically as follows:

$$\underset{\text{Copper.}}{Cu} + \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{2H_2SO_4} = \underset{\substack{\text{Copper}\\\text{Sulphate.}}}{CuSO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\substack{\text{Sulphur}\\\text{Dioxide.}}}{SO_2.}$$

(4) When the copper in the above reaction is replaced by charcoal, the gas is evolved according to the following:

$$\underset{\text{Carbon}}{C} + \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{2H_2SO_4} = \underset{\text{Water.}}{2H_2O} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{CO_2} + \underset{\substack{\text{Sulphur}\\\text{Dioxide.}}}{2SO_2.}$$

This method is not available when the gas is required absolutely pure, on account of the accompanying carbon dioxide, but for making the official **Acidum Sulphurosum** the small quantity of carbonic acid is no disadvantage.

(5) Sulphur and sulphuric acid heated together give the pure gas·

$$S + 2H_2SO_4 = 2H_2O + 3SO_2.$$

(6) When warm diluted sulphuric acid is added to a sulphite, the gas is given off freely:

$$\underset{\substack{\text{Sodium}\\\text{Sulphite.}}}{Na_2SO_3} + \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{H_2SO_4} = \underset{\substack{\text{Sodium}\\\text{Sulphate}}}{Na_2SO_4} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Sulphur}\\\text{Dioxide.}}}{SO_2.}$$

Properties.—Sulphur dioxide is a colorless gas, having a suffocating odor. One volume of water at 0° dissolves 79.8 volumes, and at 20° 39.4 volumes of the gas. When water at 0° is saturated with the gas, it deposits crystals having the formula $H_2SO_3.14H_2O$. These crystals melt at 1° to 2°, without evolution of the gas. At a temperature of —10°, or under a pressure of three atmospheres, the gas condenses to a colorless, mobile liquid, which boils at —8°, and at —76° becomes a crystalline solid.

The liquid sulphur dioxide has a specific gravity of 1.49 at 20.5°. It is manufactured by Pictet, of Geneva, and sent into commerce in copper cylinders. On the large scale, pressure affords the cheapest means of converting the gas into the liquid state, but for laboratory experiments it may be readily obtained in the liquid condition by passing it through a tube surrounded by a freezing mixture of salt and ice. The liquid may also be prepared and preserved by sealing in a strong glass tube one part of sulphur and five parts of sulphur trioxide. The reaction takes place spontaneously according to the following:

$$2SO_3 + S = 3SO_2.$$

A low temperature may be produced by the vaporization of liquid sulphur dioxide, and this may be intensified by directing a current of air over its surface.

The gas is very stable under high temperatures until 1200° are attained, when decomposition into sulphur trioxide and sulphur takes place:

$$3SO_2 = 2SO_3 + S.$$

Both gaseous and liquid sulphur dioxide, in the presence of water, possess active bleaching properties. The action in this case is a *reducing* one, the opposite to that by which chlorine accomplishes the same purpose. In the presence of organic matter it appears to have the power of decomposing water, combining with the oxygen, while the hydrogen in the nascent state is free to combine with the oxygen of the coloring matter, forming colorless compounds:

$$SO_2 + 2H_2O = H_2SO_4 + H_2.$$

The coloring matter is not destroyed, as in the case of chlorine, but may be restored by neutralizing with an alkali, hence the importance of thorough washing to remove these sulphur compounds in the process of bleaching. It is especially valuable i the bleaching of wool and silk where chlorine would injure th fabric.

With solutions of the metallic hydrates and carbonates, sulph dioxide produces sulphites according to the following reactions

$$\underset{\substack{\text{Potassium}\\\text{Hydrate.}}}{2KOH} + \underset{\substack{\text{Sulphur}\\\text{Dioxide.}}}{SO_2} = \underset{\substack{\text{Potassium}\\\text{Sulphite}}}{K_2SO_3} + \underset{\text{Water.}}{H_2O.}$$

$$\underset{\substack{\text{Potassium}\\\text{Carbonate.}}}{K_2CO_3} + \underset{\substack{\text{Sulphur}\\\text{Dioxide.}}}{SO_2} = \underset{\substack{\text{Potassium}\\\text{Sulphite.}}}{K_2SO_3} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{CO_2.}$$

Certain metallic peroxides are converted by sulphur dioxide into sulphates, as follows:

$$\underset{\substack{\text{Lead}\\\text{Peroxide.}}}{PbO_2} + \underset{\substack{\text{Sulphur}\\\text{Dioxide.}}}{SO_2} = \underset{\substack{\text{Lead}\\\text{Sulphate.}}}{PbSO_4.}$$

Iodine is converted into hydriodic acid by sulphur dioxide:

$$\underset{\text{Iodine.}}{I_2} + \underset{\substack{\text{Sulphur}\\\text{Dioxide.}}}{SO_2} + \underset{\text{Water.}}{2H_2O} = \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{H_2SO_4} + \underset{\substack{\text{Hydriodic}\\\text{Acid.}}}{2HI.}$$

In the absence of water this reaction is reversed, as follows:

$$H_2SO_4 + 2HI = I_2 + SO_2 + 2H_2O.$$

Sulphur dioxide is detected by paper which has been saturated with solutions of potassium iodate and starch. When this is brought in contact with the gas the starch is turned blue by the liberated iodine, as follows:

$$\underset{\substack{\text{Potassium}\\\text{Iodate.}}}{2KIO_3} + \underset{\substack{\text{Sulphur}\\\text{Dioxide.}}}{5SO_2} + \underset{\text{Water.}}{4H_2O} = \underset{\substack{\text{Acid}\\\text{Potassium}\\\text{Sulphate.}}}{2KHSO_4} + \underset{\substack{\text{Sulphuric}\\\text{Acid}}}{3H_2SO_4} + \underset{\text{Iodine.}}{I_2.}$$

If, however, the gas should be in excess it will react on the free iodine, according to the reaction given above for the formation of hydriodic acid, and the paper will be bleached.

Uses.—The gas is used extensively in bleaching, disinfecting, and in the manufacture of sulphurous acid and the sulphites. The cheapest source is from sulphur or iron pyrites. Its antiseptic properties are especially valuable for the preservation of meat.

SULPHUROUS ACID.

Formula, H_2SO_3 *Molecular Weight*, 81.86

Acidum Sulphurosum, U. S. P.—This acid is not known in the free state, but there are good reasons for believing that it exists in aqueous solution.

Preparation.—It is prepared by passing sulphur dioxide into water at 10°. The United States Pharmacopœia recommends that the gas be prepared from sulphuric acid and charcoal, but on a larger scale it is generally made by burning sulphur. For the details and reactions involved in the preparation of the gas, the preceding pages on sulphur dioxide may be consulted.

Properties.—The official sulphurous acid is a colorless liquid, of a sulphurous odor, and an acid, sulphurous, and somewhat astringent taste. It has the specific gravity 1.035 at 15°, and contains 6.4 per cent. of the gas by weight. It reddens litmus paper strongly, and then bleaches it. On the application of heat, all the gas is given off, and then the water volatilizes, leaving no residue. This property would serve to detect many impurities. Not more than a turbidity should be produced on adding to sulphurous acid a little barium chloride and dilute hydrochloric acid, indicating the absence of more than traces of sulphuric acid.

Sulphites.—Sulphurous acid is dibasic, that is, has two hydrogen atoms replaceable by bases. This gives rise to two series of salts, the *acid* or *bi*-sulphites, in which only one hydrogen atom is replaced, as follows :

$$\underset{\substack{\text{Potassium}\\\text{Hydrate.}}}{KOH} + \underset{\substack{\text{Sulphurous}\\\text{Acid.}}}{H_2SO_3} = \underset{\substack{\text{Potassium}\\\text{Bisulphite.}}}{KHSO_3} + \underset{\text{Water.}}{H_2O},$$

and the *normal* sulphites, in which both hydrogen atoms are replaced, as follows ·

$$\underset{\substack{\text{Potassium}\\\text{Hydrate.}}}{2KOH} + \underset{\substack{\text{Sulphurous}\\\text{Acid.}}}{H_2SO_3} = \underset{\substack{\text{Potassium}\\\text{Sulphite.}}}{K_2SO_3} + \underset{\text{Water.}}{2H_2O}.$$

The sulphites are usually prepared by passing the gas from burning sulphur into a solution of a hydrate ; the amount of gas used determines whether an acid or normal sulphite is formed. Except the sulphites of the alkali metals, they are rather insoluble in water.

Heat decomposes most of the sulphites, some into oxides and sulphur dioxide, as :

$$CaSO_3 = CaO + SO_2,$$

others into sulphates and sulphides, as :

$$4K_2SO_3 = 3K_2SO_4 + K_2S.$$

They are also decomposed on the addition of hydrochloric or sulphuric acid, evolving sulphur dioxide, and forming a chloride or sulphate of the base. The sulphite of potassium, $K_2SO_3.2H_2O$, and the bisulphite and sulphite of sodium, $NaHSO_3$ and $Na_2SO_3.7H_2O$, are official.

Detection.—The sulphites, as well as the bisulphites, are easily detected by the addition of zinc and hydrochloric acid, when hydrogen sulphide will be evolved :

$$3Zn + 6HCl + H_2SO_3 = 3ZnCl_2 + 3H_2O + H_2S.$$

The use of free hydrochloric acid is necessary, since in its absence the following reaction takes place:

$$Zn + 2H_2SO_3 = ZnSO_3 + H_2SO_2 + H_2O.$$

The salts of silver, mercury, and lead added to sulphurous acid or a sulphite produce a precipitate which blackens on heating, owing to formation of sulphide.

The sulphites and bisulphites are largely used in bleaching and disinfecting, and in addition are employed more or less in medicine.

PRACTICAL EXERCISES.

(1) In a flask, similar to that arranged for the preparation of chlorine, place a few copper turnings and cover them with concentrated sulphuric acid. Apply a gentle heat, gradually increasing until effervescence commences, and collect the resulting gas by downward displacement, as under chlorine. This gas is sulphurous oxide.

(2) A dry tube full of the gas inverted in a vessel of water will show the ready solubility of it in that liquid.

(3) A piece of moistened blue litmus paper held in the gas will at first become red, but after the lapse of some time will turn white, thus showing the bleaching property of the gas.

(4) Plunge a lighted taper into a tube full of the gas; it is quickly extinguished, indicating that the gas is neither combustible nor a supporter of combustion.

(5) Pass the gas into water until the latter smells strongly of it, then add to the resulting liquid a solution of potassium permanganate; the purple color of the latter will be destroyed as rapidly as added.

SULPHUR TRIOXIDE.

SULPHURIC OXIDE.

Formula, SO_3. *Molecular Weight*, 79.86.

Preparation.—This compound may be prepared by direct union of two volumes of sulphur dioxide with one volume of oxygen, by the aid of red-hot platinum sponge:

$$2SO_2 + O_2 = 2SO_3.$$

The white fuming compound is conducted into a well-cooled receiver where it condenses in long needles. It is important that all parts of the apparatus be free from moisture, and that the gases be previously well dried by passing them through sulphuric acid, and then through a column of pumice, moistened with the concentrated acid. This method has been so modified as to make it available for working on a large scale, by allowing concentrated sulphuric acid to fall drop by drop on pieces of red-hot bricks, when the following decomposition takes place:

$$2H_2SO_4 = 2SO_2 + O_2 + 2H_2O.$$

This mixture is freed from moisture by passing it through sulphuric acid, by which the H_2O is removed, and the remaining SO_2 and O passed over red-hot spongy platinum, to combine them into sulphuric oxide. When the fuming, or Nordhausen, sulphuric acid is carefully heated in a glass or platinum retort, sulphuric oxide distils, leaving ordinary sulphuric acid behind:

$$H_2S_2O_7 = H_2SO_4 + SO_3.$$

On heating concentrated sulphuric acid with phosphorus pentoxide, water is extracted and sulphuric oxide formed:

$$H_2SO_4 + P_2O_5 = 2HPO_3 + SO_3.$$

Properties.—Sulphur trioxide consists of long transparent prisms. When perfectly anhydrous it fuses at 14.8°, and boils at 46.2°. On standing for some time at ordinary temperatures, long crystalline fibres slowly form, which fuse at 50°. This has been termed a second modification of sulphur trioxide; it is readily converted into the first by fusing and then reducing the temperature to 14°. At the present time it is considered that there is but one form of the trioxide, the fibrous modification melting at 50° being produced by the absorption of traces of moisture.

The pure trioxide when melted has a specific gravity of 1.97 at 20°. Sulphur trioxide possesses a great affinity for water and fumes on exposure to air. When thrown on water it dissolves with a hissing noise, at the same time evolving considerable heat.

When mixed with barium oxide the following reaction takes place:

$$\underset{\substack{\text{Barium}\\ \text{Oxide.}}}{BaO} + \underset{\substack{\text{Sulphur}\\ \text{Trioxide.}}}{SO_3} = \underset{\substack{\text{Barium}\\ \text{Sulphate.}}}{BaSO_4.}$$

The evolution of heat is so great in this reaction that the mass becomes red-hot. Sulphur trioxide is manufactured on a large scale, and comes into commerce in soldered iron boxes or seale glass globes.

Uses.—It is used in the preparation of artificial alizarin, a in dissolving indigo, having replaced to a certain extent Nordhausen sulphuric acid.

SULPHURIC ACID.

Formula, H_2SO_4. *Molecular Weight*, 97.82.

History.—Geber, in the eighth century, appears to have prepared this acid in an impure state, but the first exact knowledge dates from the fifteenth century, when Basil Valentine prepared it by distilling ferrous sulphate. A crude form of the present process is said to have been introduced into England, from the Continent, in the early part of the last century, by Cornelius Drebbel. This method consisted in burning sulphur and nitre together in large glass globes, the bottoms of which were covered with water. This glass vessel was replaced by the present lead chamber, at the suggestion of Dr. Roebuck, in 1746.

Occurrence.—In the free state sulphuric acid is found in springs originating in the vicinity of volcanoes, and in certain rivers that have their sources in the Andes of South America. In combination it occurs as the sulphates of calcium, barium, magnesium, and a number of other metals.

Preparation.—The formation of sulphuric acid is based on the oxidation of sulphur dioxide in the presence of water. This takes place slowly by atmospheric oxygen, but rapidly by the oxides of nitrogen, which in turn readily take oxygen from the atmosphere.

The following reaction is the simplest expression for what takes place in the "lead chamber process:"

$$\underset{\substack{\text{Sulphur}\\\text{Dioxide.}}}{2SO_2} + \underset{\substack{\text{Nitrogen}\\\text{Tetroxide.}}}{N_2O_4} + \underset{\text{Water.}}{2H_2O} = \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{2H_2SO_4} + \underset{\substack{\text{Nitrogen}\\\text{Dioxide.}}}{N_2O_2}.$$

This reaction may be accomplished on a small scale by conducting into a large glass globe sulphur dioxide, nitrogen dioxide, steam, and air. The process will apparently go on indefinitely, since the nitrogen dioxide is reconverted into tetroxide by the oxygen of the air; but the nitrogen of the air is present in increasing amount, and so dilutes the mixture as to prevent further action until it is removed.

When the steam is not simultaneously admitted with the others there are deposited "lead chamber crystals:"

$$2SO_2 + N_2O_4 + O + H_2O = 2HSO_3NO_2,$$

which dissolve on the admission of steam, forming sulphuric acid and red fumes:

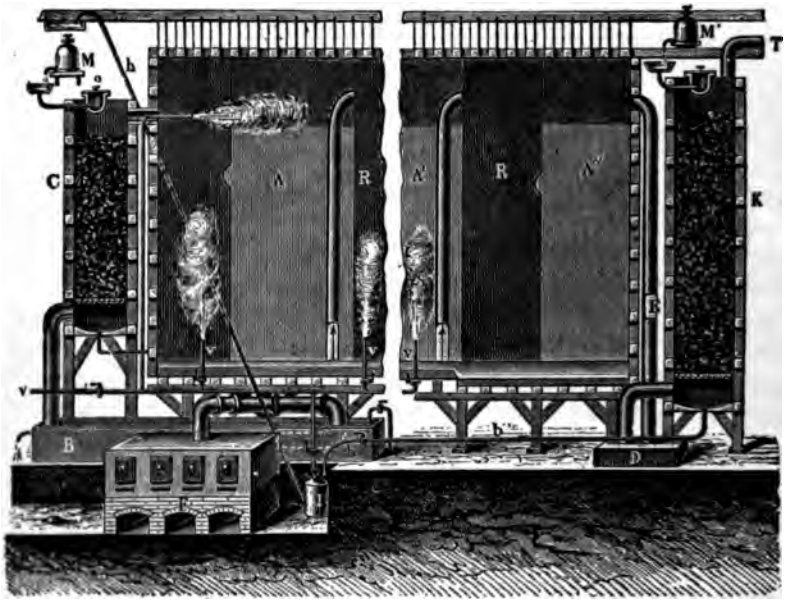
$$2HSO_3NO_2 + H_2O = 2H_2SO_4 + N_2O_3.$$

On the large scale the lead chamber process is carried out by the most economical methods, and therefore by the use of the cheapest materials. In England the sulphur dioxide is prepared by roasting pyrites, FeS_2; in the United States from pyrites, and by burning sulphur. The oxides of nitrogen are prepared by the action of sulphuric acid on Chili saltpetre.

A view of the lead chambers with the two towers is shown in Fig. 54.

The details of the process are, briefly, as follows: Sulphur dioxide, generated by one of the methods above stated, is passed into the Glover tower, C, where it is cooled and mixed with dilute sulphuric acid which trickles down over the pieces of bricks into the tower from M; at the same time from an adjoining cistern there runs down, and mixes with this, concentrated sulphuric acid containing oxides of nitrogen in solution.

FIG. 54.



Preparation of sulphuric acid.

The effect of this mixing with dilute acid is to liberate the oxides of nitrogen from the concentrated acid, which oxides, with sulphur dioxide, oxygen, nitric acid, and steam, are passed into chamber A, where the following reactions take place:

$$(1)\ SO_2 + 2HNO_3 = H_2SO_4 + N_2O_4.$$
$$(2)\ 2N_2O_2SO_2 + O_2 + 2H_2O = 2H_2SO_4 + 2N_2O_3.$$

From the first chamber the uncombined gases pass into a second chamber where further combination and condensation take place, and in a third chamber the condensation is completed so that only oxides of nitrogen and nitrogen gas escape into the Gay-Lussac tower, K. In this latter tower the oxides are dissolved by concentrated sulphuric acid from M, trickling down over pieces of coke.

When this concentrated acid reaches the bottom, saturated with oxides of nitrogen, it is transferred by suitable pipes to the top of the Glover tower to run down and mix with fresh quantities of dilute acid and sulphur dioxide. The concentrated acid for the Gay-Lussac tower is taken from the bottom of the Glover tower, as the mixed dilute and strong acids in meeting with the hot gases have been deprived of nearly all water.

The circulation of gases through the system of towers and chambers is maintained by the draught of a tall chimney.

It will be seen that the same sulphuric acid is repeatedly used and nearly all the oxides of nitrogen are saved, so that the process consists in generating a continuous supply of sulphur dioxide with a small quantity of nitric acid to make up the loss which is unavoidable. The principal supply of oxygen comes from the atmosphere.

The furnace in which the sulphur or pyrites is burned is so arranged as to furnish the necessary heat for the decomposition of the nitrate.

The acid in the bottom of the lead chamber is drawn off when it attains a specific gravity of 1.55 to 1.60,—containing 64 per cent. of absolute sulphuric acid. If allowed to become more concentrated than this it begins to absorb nitrous fumes. It is then concentrated in leaden pans until it reaches the specific gravity of 1.75, containing 78 per cent. of the acid, when it commences to attack the lead, and is, therefore, transferred to vessels of iron, glass, or, best of all, platinum, to be finally concentrated or distilled. Even platinum is slowly attacked by the acid, so that recently it has been found advantageous to line these platinum stills with gold.

The lead chamber process has been carried to the highest development in England, where the annual production of the acid is nearly one million tons.

Theoretically 100 parts of sulphur should yield 305.9 parts of sulphuric acid, but in practice this is never quite reached. 290 parts are about the average, and in some of the best works 297 parts are attained.

The amount of sodium nitrate required also varies. In manufactories where both the Gay-Lussac and Glover towers are used, only 3.5 to 7.5 parts of the nitre are found necessary for every 100 parts of sulphur.

Sulphuric acid, when prepared without distillation, is dark in color and contains lead sulphate, arsenic, and nitrogen trioxide. The arsenic may be removed by adding a small quantity of hydrochloric acid and boiling, when arsenous chloride will pass off; the nitrogen trioxide may be removed by the addition of ammonium sulphate, when the following reaction takes place with evolution of nitrogen:

$$(NH_4)_2SO_4 + N_2O_3 = H_2SO_4 + 3H_2O + 2N_2.$$

Finally, to remove lead and any other fixed impurities, the acid is distilled from glass or gold-lined platinum retorts. When one-third of the acid has passed over, the receiver is changed and the remainder, distilled nearly to dryness, furnishes the pure, colorless acid.

Properties.—When pure, sulphuric acid is a colorless, oily, inodorous, corrosive liquid of the specific gravity 1.840, and containing not less than 96 per cent. of absolute H_2SO_4. When all but 2 per cent. of water has been removed and the acid cooled, crystals of pure H_2SO_4 separate out, which melt at 10.5°. These crystals, when melted, will frequently retain the liquid condition considerably below the solidifying point; when, however, the liquid is agitated, or a crystal is added, the mass solidifies, and the temperature rises to 10.5°. The pure liquid has the specific gravity 1.854 at 0°, and 1.834 at 24°, compared with water at the same temperatures.

Acidum Sulphuricum, U. S. P., has a specific gravity of 1.835 at 15°, and contains 92.5 per cent. by weight of absolute H_2SO_4. On heating the absolute acid it begins to fume at 30°, sulphur trioxide escaping. This evolution of the trioxide continues until the temperature reaches 338°, and is maintained at that, when a liquid distils over unchanged containing 98.4 to 98.8 per cent. of H_2SO_4. On diluting with water until the acid has the specific gravity 1.78 and the composition $H_2SO_4 + H_2O$, the so-called monohydrated acid crystallizes at 0°, and the crystals melt at 7.5°.

Sulphuric acid has a strong affinity for water, and when mixed with it great heat is developed. In diluting, the acid should always be poured into the water, slowly and with constant stirring; when the reverse is attempted the acid is liable to be thrown out by the violent ebullition resulting from the sudden rise in temperature. The mixing is accompanied by diminution of volume, the maximum contraction amounting to 8 per cent. when one molecule of the acid is mixed with two of water. On account of this affinity for water, organic substances are rapidly decomposed, hydrogen and oxygen in the proportion to form water being removed, and carbon, in many compounds, separating out. An example of this occurs when sulphuric acid is added to sugar. The concentrated acid does not so readily attack metals as that which is more diluted. In some cases the metal becomes coated with a layer of sulphate, which prevents further action. This is notably the case with zinc and iron. Copper, mercury, antimony, bismuth, lead, and silver are dissolved on heating with the acid, a reduction of the latter taking place with an evolution of sulphur dioxide at the same time. Gold, platinum, and some other of the noble metals are not appreciably affected even by boiling with the acid. For this reason the latter when concentrated may be used to separate silver from gold.

Uses.—Sulphuric acid is consumed in all branches of chemical industry. Perhaps its most extensive use is in the Leblanc soda industry, where the chamber acid is employed without concentration. It is also largely consumed in the refining of petroleum, in the manufacture of fertilizers, in making parchment, in the conversion of starch into glucose, and in the manufacture of carbon dioxide from calcium carbonate.

Tests and Impurities.—Sulphuric acid and sulphates are detected by giving a white precipitate with barium chloride, insoluble in hot concentrated acids; also by the white precipitate which they form with salts of lead, insoluble in dilute acids, but soluble in hot concentrated acids. Sulphates may also be detected by heating a fragment on charcoal with sodium carbonate and moistening the fused mass on a silver coin with a drop of diluted hydrochloric acid, when a dark stain of silver sulphide will be produced. This is known as the *Hepar* [illegible].

Sulphuric acid is liable to contain lead, nitric acid, or nitrogen trioxide, arsenic, selenium, and organic matter. It should volatilize from a glass or platinum dish at a temperature of 350° without residue. Lead is detected on diluting with water, or, better, with alcohol, when a precipitate of lead sulphate will take place. When some of the acid in a test-tube is covered with a layer of ferrous sulphate solution, no dark ring should be formed at the point of contact of the two liquids, indicating the absence of *nitric acid* and the *oxides of nitrogen*. When considerably diluted with water and treated with pure zinc it evolves a gas which should not blacken paper moistened with solution of silver nitrate, indicating the absence of *arsenic* or *sulphurous acid*.

When the acid is mixed with twice its volume of water, the mixture added to half its bulk of sulphurous acid, and then allowed to stand, no red color of separated selenium should occur, according to the following reaction:

$$\underset{\text{Selenous Acid.}}{H_2SeO_3} + \underset{\text{Sulphurous Acid.}}{2SO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Sulphuric Acid.}}{2H_2SO_4} + \underset{\text{Selenium.}}{Se.}$$

Organic matter is recognized by the dark color it imparts to the acid.

Sulphates.—Sulphuric acid forms two series of salts, the *neutral* or *normal* sulphates, in which both hydrogen atoms of the acid are replaced by a base, as Na_2SO_4, and the *acid* sulphates, in which only one hydrogen atom is replaced by a base, as $NaHSO_4$. Most of the sulphates are soluble in water, the important exceptions being those of barium, strontium, calcium, and lead. The sulphates of sodium, ammonium, iron, and certain alkaloids have extensive use in medicine.

NORDHAUSEN OR DISULPHURIC ACID, $H_2S_2O_7$.

This is the oldest of the sulphuric acids, and was originally manufactured in the vicinity of Nordhausen, Germany, by the distillation of dried ferrous sulphate in earthen retorts:

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3.$$

There is also a small quantity of water necessarily present, since ferrous sulphate retains one molecule of water until decomposition begins; therefore a weak acid is first formed which carries with it most of the sulphur dioxide, and should be rejected. The distillate is saved when the white fumes of the trioxide make their appearance. There is still enough moisture present to make a liquid acid of a composition corresponding to the above formula.

At the present time most of the acid is made in Bohemia. The operation is commenced by roasting pyrites, by which ferrous sulphate and basic ferric sulphate, $Fe_2S_2O_9$, are formed. On lixiviating the mass a solution of the sulphates is obtained, which, on evaporation and ignition, gives a residue of the basic sulphate alone. The presence of the ferrous salt is avoided as far as possible on account of the formation of sulphur dioxide as above given. On submitting the basic salt to distillation the following reaction takes place:

$$Fe_2S_2O_9 = Fe_2O_3 + 2SO_3.$$

The residue is the *caput mortuum* or *colcothar* used in polishing. The acid is also prepared by dissolving sulphur trioxide in concentrated sulphuric acid:

$$H_2SO_4 + SO_3 = H_2S_2O_7.$$

This would require about 45 per cent. of the trioxide, but the commercial acid often contains less than 20 per cent. of it.

Properties.—Fuming sulphuric acid is a thick, oily liquid, colorless when pure, but often of a brownish color from small quantities of organic matter. As ordinarily found, its specific gravity is rarely above 1.865. Since the introduction of the trioxide into commerce the liquid may be obtained in sealed tubes or bulbs. It is of semi-solid consistence, and of the specific gravity 1.900. When the acid is cooled, large crystals separate, which are of a white color and melt at 35°.

Disulphuric acid forms both acid and normal salts; for example, with sodium we have $NaHS_2O_7$ and $Na_2S_2O_7$.

The Nordhausen acid has not any use in pharmacy, but is employed largely in the arts for dissolving indigo and in the preparation of artificial alizarin.

THIOSULPHURIC ACID, $H_2S_2O_3$.

This acid is not known in the free state, but only in combination in certain salts, of which sodium thiosulphate, $Na_2S_2O_3.5H_2O$, is the most important. The salt is improperly called hyposulphite of sodium, and consequently the acid is also miscalled hyposulphurous acid, a name which belongs to the compound H_2SO_2.

Preparation.—The sodium salt is prepared by boiling together sulphur and sodium sulphite:

$$Na_2SO_3 + S = Na_2S_2O_3.$$

It is also formed when sulphur dioxide is passed into a solution of sodium sulphide, the reaction taking place in two stages according to the following:

$$(1)\ 3SO_2 + 2Na_2S = 2Na_2SO_3 + 3S.$$
$$(2)\ Na_2SO_3 + S = Na_2S_2O_3.$$

On adding iodine to a solution of sodium sulphide and sulphite, the thiosulphate is formed as follows:

$$Na_2S + Na_2SO_3 + I_2 = Na_2S_2O_3 + 2NaI.$$

When sodium, or calcium, pentasulphide is exposed to the air, it absorbs oxygen and is converted into thiosulphate:

$$Na_2S_5 + 3O = Na_2S_2O_3 + 3S.$$

In case the calcium salt is formed, it may be converted into the sodium salt by the addition of sodium carbonate. The lime used in purifying illuminating gas, and known as *gas lime*, contains calcium pentasulphide and hyposulphite. This is exposed to the air, whereby the sulphide is converted into thiosulphate, the mass is lixivated with water, and the solution, by double decomposition with sodium carbonate, gives calcium carbonate and sodium thiosulphate, as follows:

$$CaS_2O_3 + Na_2CO_3 = CaCO_3 + Na_2S_2O_3.$$

This and the *ball soda*, the waste from the manufacture of sodium carbonate, are the sources of the commercial sodium thiosulphate. Another method, which is sometimes employed on a small scale, consists in taking three parts of dried sodium carbonate and one part of sulphur, heating together in a porcelain dish to the fusing point of the sulphur, and stirring to facilitate contact with the air. Sodium sulphide is first formed, which by contact with the air is oxidized to sulphite; this is then dissolved in water and boiled with more sulphur, forming the thiosulphate according to the above reactions.

Properties.—Sodium thiosulphate occurs in large, colorless, transparent, monoclinic prisms or plates, efflorescent in dry air, odorless, having a cooling, somewhat bitter and sulphurous taste, and a neutral or faintly alkaline reaction. It is soluble in 1.5 parts of water at 15°, and in 0.5 part of boiling water, in the latter case with partial decomposition. The salt is insoluble in alcohol. When rapidly heated it melts at 50°, and on increasing the temperature to 100° it loses all its water (36.3 per cent.). The aqueous solution dissolves oxide or chloride of silver, and discharges the color of iodine solution and iodized starch.

When a solution of thiosulphate is treated with an acid, sulphur dioxide is given off and sulphur is precipitated:

$$Na_2S_2O_3 + 2HCl = 2NaCl + SO_2 + S + H_2O.$$

This reaction serves to distinguish the thiosulphates from the sulphites.

DITHIONIC ACID, $H_2S_2O_6$.

Preparation.—When sulphur dioxide is passed into water in which manganese dioxide is suspended, the following reaction takes place:

$$MnO_2 + 2SO_2 = MnS_2O_6.$$

Some manganous sulphate is formed at the same time. The solution is next treated with barium sulphide:—

$$MnS_2O_6 + BaS = MnS + BaS_2O_6.$$

On adding sulphuric acid to this, the dithionic acid is obtained in solution:

$$BaS_2O_6 + H_2SO_4 = BaSO_4 + H_2S_2O_6.$$

The solution may be concentrated in a vacuum over sulphuric acid, until it reaches the specific gravity 1.347, when further evaporation resolves it into sulphur dioxide and sulphuric acid:

$$H_2S_2O_6 = SO_2 + H_2SO_4.$$

Dithionic acid is also formed when a dilute solution of iodine in potassium iodide is added to a solution of acid sodium sulphite:

$$2NaHSO_3 + I_2 = H_2S_2O_6 + 2NaI.$$

The dithionates are not so easily oxidized as the thiosulphates. On heating, however, they are decomposed into sulphur dioxide and sulphite. They do not precipitate sulphur on the addition of hydrochloric acid and heating; this distinguishes them from the thiosulphates.

TRITHIONIC ACID, $H_2S_3O_6$.

Preparation.—When sublimed sulphur and a strong solution of acid potassium sulphite are digested at a temperature of from 50° to 60°, the potassium salt of trithionic acid is formed, as follows:

$$6KHSO_3 + S_2 = 2K_2S_3O_6 + K_2S_2O_3 + 3H_2C.$$

When a concentrated solution of potassium thiosulphate is saturated with sulphur dioxide, potassium trithionate is formed:

$$2K_2S_2O_3 + 3SO_2 = 2K_2S_3O_6 + S.$$

On adding iodine to a solution of sodium thiosulphate and sulphite, sodium trithionate is produced:

$$Na_2S_2O_3 + Na_2SO_3 + I_2 = Na_2S_3O_6 + 2NaI.$$

When the potassium salt, obtained in the second method, is treated with hydrofluosilicic acid the free acid is produced:

$$K_2S_3O_6 + SiF_4.2HF = H_2S_3O_6 + \text{[illegible]} 2KF.$$

This diluted acid allows of only moderate concentration in a vacuum, for it readily decomposes into sulphur, sulphur dioxide, and sulphuric acid. The potassium salt is the only one which is well known.

TETRATHIONIC ACID, $H_2S_4O_6$.

Preparation.—The sodium salt of this acid is formed when iodine is added to an aqueous solution of sodium thiosulphate:

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

The free acid may be prepared by carefully decomposing barium tetrathionate with diluted sulphuric acid. The diluted acid may be boiled, but on concentrating decomposition takes place, as follows:

$$H_2S_4O_6 = H_2SO_4 + SO_2 + S_2.$$

PENTATHIONIC ACID.

When hydrogen sulphide is passed into a solution of sulphur dioxide, pentathionic acid results, with separation of sulphur:

$$5H_2S + 5SO_2 = H_2S_5O_6 + 4H_2O + 5S.$$

The solution is milky, and is best cleared by digesting with metallic copper. Any copper which is dissolved is precipitated by hydrogen sulphide.

The solution may be concentrated to a specific gravity of 1.6, when it commences to evolve sulphur dioxide.

COMPOUNDS OF SULPHUR AND OXYGEN WITH CHLORINE AND BROMINE.

THIONYL CHLORIDE, $SOCl_2$.

This compound is prepared by passing dry sulphur dioxide over phosphorus pentachloride:

$$\underset{\substack{\text{Sulphur}\\\text{Dioxide.}}}{SO_2} + \underset{\substack{\text{Phosphorus}\\\text{Pentachloride.}}}{PCl_5} = \underset{\substack{\text{Thionyl}\\\text{Chloride.}}}{SOCl_2} + \underset{\substack{\text{Phosphorus}\\\text{Oxychloride.}}}{POCl_3}.$$

It is a colorless liquid, with a pungent odor, and fumes in contact with air. It boils at 78°, and has a specific gravity at 0° of 1.675. When brought in contact with water it is decomposed, as follows:

$$SOCl_2 + 2H_2O = H_2SO_3 + 2HCl.$$

SULPHURYL-HYDROXYL-CHLORIDE, OR CHLORSULPHONIC ACID, $SO_2(OH)Cl$.

This compound is formed by the action of hydrochloric acid on sulphur trioxide:

$$HCl + SO_3 = SO_2(OH)Cl.$$

It may also be obtained by distilling a mixture of sulphuric acid and phosphorus oxychloride:

$$\underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{2H_2SO_4} + \underset{\substack{\text{Phosphorus}\\\text{Oxychloride.}}}{POCl_3} = \underset{\substack{\text{Chlorsulphonic}\\\text{Acid.}}}{2SO_2(OH)Cl} + \underset{\substack{\text{Metaphosphoric}\\\text{Acid.}}}{HPO_3} + \underset{\substack{\text{Hydrochloric}\\\text{Acid.}}}{HCl.}$$

It is a colorless, fuming liquid, having a specific gravity of 1.766 at 18°, and boiling at 158°. Water decomposes it with violence, according to the following reaction:

$$SO_2(OH)Cl + H_2O = H_2SO_4 + HCl.$$

SULPHURYL CHLORIDE, SO_2Cl_2.

This substance may be prepared by direct union of sulphur dioxide and chlorine in sunlight.

It is a colorless, fuming liquid, with a suffocating odor. It boils at 70°, and has a specific gravity of 1.659 at 20°. Water decomposes it into sulphuric and hydrochloric acids.

SULPHURYL BROMIDE, SO_2Br_2.

This compound is similar to the sulphuryl chloride, and may be considered as derived from sulphuric acid by the replacement of the two hydroxyls by bromine. It is prepared by the direct union of sulphur dioxide and bromine in sunlight:

$$SO_2 + Br_2 = SO_2Br_2.$$

It is a volatile, white, crystalline solid.

SELENIUM.

Symbol, Se. *Atomic Weight*, 78.87. *Valence*, II.

History.—Selenium was discovered in 1817 by Berzelius, in the deposits from sulphuric acid chambers, and named from σελήνη, the moon.

Occurrence.—It is widely distributed in small quantities associated with sulphur.

Preparation.—This element is most conveniently prepared from lead chamber deposits. The crude material is mixed with sufficient sulphuric acid to make a paste, heated to the boiling point, and treated with nitric acid from time to time, until the red color disappears. The solution, which now contains selenic acid, H_2SeO_4, is, when cold, poured off from the sediment and saturated with sulphur dioxide, when selenium separates out as a red powder.

Thus prepared it contains lead, and sometimes other metals, from which it may be purified by distillation or by fusing with potassium nitrate and sodium carbonate, forming sodium selenate, from which it is precipitated as a red powder by hydrochloric acid.

Another method is to evaporate the solution of selenic acid, obtained as above, to remove nitric acid, and then boil with concentrated hydrochloric acid, by which the selenic acid is reduced to selenous acid, as follows:

$$H_2SeO_4 + 2HCl = Cl_2 + H_2O + H_2SeO_3.$$

The solution containing selenious acid is then saturated with sulphur dioxide, when selenium separates out according to the following reaction:

$$H_2SeO_3 + 2SO_2 + H_2O = 2H_2SO_4 + Se.$$

Selenium may also be prepared by digesting the lead chamber deposit on a water bath with a concentrated solution of potassium cyanide:

$$KCN + Se = SeKCN.$$

From this solution the selenium is deposited, in red flakes, on the addition of hydrochloric acid. The residue may be purified by distillation, or by fusion as previously described.

Properties.—Like sulphur, selenium exists in different allotropic modifications.

(1) The amorphous form, soluble in carbon disulphide.

This variety is obtained by quickly cooling the molten selenium. It exists as an amorphous, nearly black mass, of the specific gravity 4.3.

(2) From the solution of the above amorphous variety in carbon disulphide dark-red, monoclinic crystals separate. These crystals have a specific gravity of 4.5, and are isomorphous with the monoclinic crystals of sulphur.

(3) When the amorphous variety is warmed for some time at 97° it is converted into a lead-gray, crystalline mass, which is insoluble in carbon disulphide and has the specific gravity of 4.5.

(4) If a concentrated solution of sodium or potassium selenide be exposed to the air for some time, black microscopic crystals of metallic selenium separate, which have a specific gravity of 4.8. The first and second varieties change at from 90° to 100° into the third, and the second, third, and fourth, when melted and quickly cooled, change to the first. The varieties which dissolve in carbon disulphide soften and melt so slowly that no constant melting point can be assigned to them. The insoluble varieties melt at 217°. All the different forms boil at about 700°, forming a reddish yellow vapor, which may be condensed in scarlet powder. Like sulphur, the vapor density of selenium decreases as the temperature rises. At 1400° it possesses the normal density corresponding to the formula Se_2.

When heated in the air, selenium burns with a bright blue flame, yielding selenium dioxide, SeO_2. The vapor has an odor resembling horse-radish.

The compounds of selenium are very similar to those of sulphur. Hydrogen selenide is a very irritating, disagreeably-smelling gas. One oxygen compound, SeO_2, two acids, selenous and selenic, are known, as well as a series of interesting compounds known as *selenosulphates*, in which selenium replaces some of the sulphur in thiosulphates. Selenic acid, H_2SeO_4, corresponding to sulphuric acid, H_2SO_4, resembles the latter in many respects, but has one characteristic property not possessed by any other acid, namely, that of dissolving gold,—the selenic being reduced to selenous acid at the same time.

The compounds of selenium are best detected by the red precipitate of the element which occurs on the addition of sulphurous acid or sulphur dioxide.

TELLURIUM.

Symbol, Te. *Atomic Weight*, 125. *Valence*, II.

History.—Tellurium was discovered in 1782 by Müller von Reichenstein, and more fully investigated by Klaproth and Berzelius. It was named tellurium by Klaproth from *tellus*, the earth.

Occurrence.—This element occurs sparingly in the free state, and as tellurides of gold, silver, lead, bismuth, and mercury in California, Colorado, Brazil, and Hungary.

Preparation.—Bismuth telluride is fused with sodium carbonate. The resulting telluride of sodium, still mixed with a small quantity of sulphide, is dissolved in water and exposed to the air, by which the metal is precipitated. It is then purified by distillation in a stream of hydrogen.

Properties.—Tellurium is a silver-white metal of a brittle texture, and has a specific gravity of 6.24. It melts at about 500°, and volatilizes at about 1300°, yielding yellow vapors. It is insoluble in carbon disulphide, but dissolves in concentrated sulphuric acid, imparting a deep-red color to the solution, from which it is precipitated on the addition of water.

On heating in the air, it burns with a blue flame, yielding white fumes of tellurium dioxide.

Tellurium forms many compounds corresponding to those of selenium and sulphur. They are recognized by fusing with potassium carbonate, by which potassium telluride is formed, which dissolves in water with a red color, and, on the addition of hydrochloric acid, yields the disagreeably-smelling compound, hydrogen telluride.

CHAPTER V.

THE NITROGEN GROUP.

NITROGEN.

Symbol, N. *Atomic Weight*, 14.01. *Valence*, III.

History.—The fact that something existed in the atmosphere which would not support life appears to have been observed in 1772 by Dr. Rutherford, Professor of Botany in the University of Edinburgh. He confirmed the correctness of his observation by treating the air which had been breathed by animals with potassium hydrate to remove carbon dioxide, and then found that the residue would not support life or combustion. In consequence of this he is usually given the credit of having discovered the element. About the same time the composition of air was investigated by Priestley, Scheele, Lavoisier, and Chaptal. The last suggested the present name, from *νίτρον*, nitre, and *γενναω*, I produce, since it was found to be a constituent of saltpetre. Lavoisier suggested the name *azote*, which is still retained by the French, with the symbol Az, the symbol N being used by all other nations.

Occurrence.—In the free state nitrogen constitutes four-fifths of the atmosphere. In combination with sodium and oxygen, it occurs in enormous quantities as Chili saltpetre. Animal and vegetable substances always contain a distinct quantity of it.

Preparation.—(1) Nitrogen may be prepared by removing the oxygen from the air. This is accomplished by attaching a porcelain crucible or crucible lid to a cork so that the two will float on water. The phosphorus is placed on the porcelain, ignited, and a bell-jar immediately brought over the whole, so as to rest with its rim below the surface of the water. The phosphorus is extinguished so soon as the oxygen is all consumed, and after cooling the water rises and fills one-fifth the volume of the jar. The remaining four-fifths are nearly pure nitrogen. The white fumes given off during the combustion are phosphorus pentoxide, and are rapidly dissolved by the water. The residue on the crucible lid consists of some uncombined phosphorus with phosphorus trioxide.

(2) Nitrogen may also be prepared by removing the oxygen

rom the atmosphere with red-hot copper. The copper is heated o redness in a glass or porcelain tube, and air, previously purified by passing it over sulphuric acid and potassium hydrate to remove organic impurities, moisture, and carbon dioxide, is passed over it; almost pure nitrogen results, which may be collected over mercury, or over water if a very little moisture be no objection.

(3) When chlorine is passed into solution of ammonium hydrate, nitrogen is evolved:

$$8NH_3 + 3Cl_2 = 6NH_4Cl + N_2.$$

It is very important to keep the ammonia in excess, for, should the amount of chlorine exceed that of ammonia, the dangerously explosive nitrogen chloride will form. This process is not to be recommended when we have so many safer and simpler ones.

(4) Solutions of ammonium nitrate and ammonium chloride heated together evolve both chlorine and nitrogen, according to the following reaction:

$$4NH_4NO_3 + 2NH_4Cl = 5N_2 + Cl_2 + 12H_2O.$$

The chlorine may be removed by passing the resulting mixed gases through sodium hydrate solution or milk of lime,

(5) Ammonium dichromate when heated evolves nitrogen:

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2.$$

The ammonium dichromate for the above method is formed when potassium dichromate and ammonium chloride are heated together, and is immediately decomposed. The whole reaction may be expressed as follows:

$$K_2Cr_2O_7 + 2NH_4Cl = Cr_2O_3 + 2KCl + 4H_2O + N_2.$$

(6) A similar method consists in heating ammonium nitrite:

$$NH_4NO_2 = 2H_2O + N_2.$$

The ammonium salt in this, as in the preceding, case is decomposed at the moment of its formation, in this method the cheaper and more available materials being potassium nitrite and ammonium chloride:

$$KNO_2 + NH_4Cl = KCl + N_2 + 2H_2O.$$

The gas may be evolved from the dry salts, but it comes off with greater regularity when they are previously dissolved in a little water.

Properties.—Nitrogen is a colorless, tasteless, and inodorous gas. Its density is 14, making it a trifle lighter than air. It is very slightly soluble in water, 100 volumes of the liquid absorbing 1.5 volumes of the gas at 12.66° ; it is somewhat more soluble in alcohol.

Under a pressure of 35 atmospheres and a temperature of —146° nitrogen liquefies. In this liquid state it has a specific gravity of 0.885, boils at —194.4, and solidifies at —214°.

Nitrogen is neither combustible nor a supporter of combustion. In the free state it is remarkably inactive toward all other elements ; but its compounds, which are always formed by indirect means, are in nearly all cases very active ; many of them, the alkaloids and cyanides, for example, being especially active physiologically.

Uses.—Nitrogen is useful in carrying out such chemical operations as require the exclusion of oxygen.

THE ATMOSPHERE.

History.—Air was considered one of the elements by the ancients, but this idea was broken down when oxygen was discovered by Priestley and nitrogen by Rutherford, over a century ago ; and the relation of these two elements to the atmosphere was investigated by Lavoisier and Cavendish.

Distribution.—Air exists at the surface of the earth and to an unknown height above it. It is estimated by some to be a layer forty-five miles and by others two hundred miles in thickness.

On account of its being an elastic body it will be denser at the sea-level ; consequently we must consider it to be at a height of forty-five miles a gas of extreme tenuity. The time during which twilight is visible in the zenith has given the basis on which the calculation of forty-five miles has been made ; but it has been observed that meteors ignite at a distance of about two hundred miles above the earth's surface, thus rendering it probable that there is some resistance at that height.

Weight.—Pure dry air is 14.44 times heavier than hydrogen, consequently one liter at 0° and 760 millimeters pressure weighs 1.2932 gramme. The pressure of the atmosphere at the sea-level is, therefore, very nearly fifteen pounds on every square inch of surface, equal to a column of mercury at 0°, 760 millimeters in height. This pressure rapidly diminishes as we ascend from the sea-level.

Composition.—The atmosphere is made up of seventy-nine volumes of nitrogen and twenty-one volumes of oxygen. There are always present small quantities of water, carbon dioxide, ammonium carbonate, ammonium nitrate, sodium chloride, and particles of floating matter generally known as dust. By weight the proportion is 77 per cent. of nitrogen and 23 per cent. of oxygen. The proportion of carbon dioxide is variable, being on an average 0.03 per cent., but is found in cities often as high as 0.11 per cent. The amount of aqueous vapor is still more variable, and is affected by local causes, as temperature and altitude; the average is estimated at about 0.75 per cent. When air is freed from carbon dioxide and water vapor, the proportion of nitrogen to oxygen is found to be remarkably constant. All the great number of analyses made of air during the past fifty years, by many different investigators, show but slight variations from the figures above given, although the samples have been taken from all parts of the globe and from elevations of fourteen thousand feet. The constancy of these proportions led some of the earlier chemists to believe that air was a compound of oxygen and nitrogen, but in view of certain properties we must conclude that it is a mechanical mixture.

Properties.—The following are some of the characters which prove it to be a mixture:

(1) The physical and chemical properties of a mixture of seventy-nine volumes of nitrogen and twenty-one volumes of oxygen are exactly the same as air. When the two gases are mixed there is no evidence of chemical action, the temperature of the mixture remaining the same as that of the constituents.

(2) The proportion in which the two elements exist in air bears no relation to their atomic weights, and this proportion has been found to vary beyond the reasonable error of analysis, while a chemical compound does not vary in the proportion of its constituents.

(3) When air is drawn through a thin layer of caoutchouc, that which passes through is composed of about forty-two volumes of oxygen and fifty-eight volumes of nitrogen, on account of the property that oxygen has of passing through this medium more rapidly than nitrogen.

(4) On agitating air with water until the latter is saturated, the composition of the dissolved gas is found to be different from that of the original air on account of the solubility of oxygen in water being greater than that of nitrogen.

The question naturally suggests itself, whether the continual pouring into the atmosphere of so much carbon dioxide from all sources, the animal life on the globe as well as the product of so much decay and combustion, has not changed the composition of the air by reducing the percentage of oxygen. In reply to this it may be said that calculations based on the inhabitants at one thousand millions, and the amount of oxygen used in other ways at ten times that consumed by human beings, demonstrate that in eighteen hundred years the proportion of oxygen in the air would be decreased by only 0.1 per cent.

Analysis.—Moisture is determined by passing known quantities of air over calcium chloride and noting the increase in weight of the latter. Carbon dioxide is estimated in the same manner, using potassium hydrate instead of calcium chloride, or the air is passed into solution of barium hydrate and the resulting barium carbonate filtered off and weighed. Oxygen is estimated by taking a definite volume of pure dry air in a eudiometer tube over mercury, adding a measured volume of pure hydrogen, and exploding the mixture by means of an electric spark. After cooling there will be a contraction equal to the volume of hydrogen and oxygen which have combined, the resulting volume of water being so small as to be disregarded.

Other less accurate methods have been used, but none of them are capable of the same exactness as the above. One of these is to pass the air over red-hot copper which will combine with the oxygen. By weighing the copper before and after the operation, and weighing or measuring the nitrogen, the proportion of the two gases may be estimated. Phosphorus has also been used for removing the oxygen. When this is carried out in a tube over mercury the resulting volume of nitrogen may easily be read off.

While the composition of air under ordinary circumstances is constant, it may in crowded halls and rooms become charged with injurious amounts of carbon dioxide and other compounds from the exhalations of the individuals present. The remedy for this is perfect ventilation, which consists in removing the impure air as well as in admitting that which is pure. Once in the outside atmosphere, the impurities rapidly disappear by diffusion and by the oxidizing action of ozone and hydrogen peroxide.

PRACTICAL EXERCISES.

(1) Place a small piece of phosphorus in a little porcelain crucible, set them in a shallow vessel of water, so the phosphorus will not be wet, and ignite it by touching it with the hot end of a file or other convenient metal. Immediately bring over the crucible with its edge dipping into the water a large beaker or bell-jar. Some of the air is at first expelled by

the heat, but the oxygen is rapidly consumed and the phosphorus ceases to burn. When the apparatus is cooled the water rises in the beaker or bell-jar and occupies the amount of space previously held by the oxygen, the remaining space is filled with nitrogen.

(2) Prepare a larger quantity of nitrogen by heating, in a suitable flask, potassium nitrite dissolved in a solution of ammonium chloride. When the reaction begins, the heat must be removed, or carefully regulated to prevent too rapid evolution of the gas. Nitrogen may be collected over water like oxygen or hydrogen. The negative properties possessed by it may be noted during collection.

NITROGEN AND HYDROGEN.

AMMONIA.

Formula, NH_3. *Molecular Weight*, 17.01.

History.—Ammonium chloride, or sal ammoniac, appears to have been known from the earliest times, and the aqueous solution of the gas was described by the alchemists under the name of "spirits of hartshorn." Priestley, in 1774, was the first to prepare gaseous ammonia, by heating together sal ammoniac and lime, and collecting the gas over mercury. He gave to this gas the name of "alkaline air," which later became "volatile alkali."

Occurrence and Formation.—Ammonia, in combination with carbonic, nitric, and nitrous acids, exists in the air in minute quantities, being produced by the decomposition of organic matter. It is found in the Tuscan lagoons, probably combined with boron nitride, BN. It is also found as sulphate and chloride near active volcanoes, having been produced by the hot lava flowing over fertile soil containing nitrogen. Ammonia and its salts are formed in the dry distillation of many organic substances.

Formerly horns, hoofs, urine, and other animal products were distilled, and the ammonium carbonate thus produced neutralized with hydrochloric acid, the product after sublimation being known as sal ammoniac. At the present time our supply is obtained by a similar process, in which, however, coal is the material used. Bituminous coal yields on distillation about 2 per cent. of ammonia, which, therefore, occurs in the ammoniacal liquor formed during the manufacture of illuminating gas. In addition to free ammonia there are present in this ammoniacal gas-liquor the carbonate, sulphide, sulphate, and thiosulphate. The gas-liquor is usually distilled with lime, by which the ammonia is liberated and collected in a suitable receiver with some water. This distillate is neutralized with hydrochloric or sulphuric acid, and the resulting ammonium chloride or sulphate purified and used for preparing the other ammonium salts.

Ammonia is also formed by the action of nascent hydrogen on nitrous or nitric acid. Finally, ammonia is produced in minute quantity by passing the electric spark through a mixture of nitrogen and hydrogen. It has been said that the elements do not unite directly, and this appears to be an insignificant exception to that statement. It is improbable that such combination should take place to any great extent, since ammonia gas is decomposed by the electric spark into its constituents.

Preparation.—Ammonia gas is prepared on a large scale by heating together in a glass or iron retort calcium hydrate and ammonium sulphate or chloride :

$$\underset{\substack{\text{Ammonium}\\\text{Sulphate.}}}{(NH_4)_2SO_4} + \underset{\substack{\text{Calcium}\\\text{Hydrate.}}}{Ca(OH)_2} = \underset{\substack{\text{Calcium}\\\text{Sulphate.}}}{CaSO_4} + \underset{\text{Ammonia.}}{2NH_3} + \underset{\text{Water.}}{2H_2O}$$

For laboratory purposes it is usually preferable to heat the solution of ammonia which is supposed to contain ammonium hydrate :

$$NH_4OH = NH_3 + H_2O.$$

When required pure the gas must be passed over calcium oxide (quicklime) to remove moisture, and collected over mercury. As ordinarily needed it may be collected by "upward displacement;" that is, by holding an inverted vessel over the tube from which the gas is escaping, which gas, being lighter than air, rises and fills the vessel.

Properties.—Ammonia is a colorless gas, of a pungent, suffocating odor and a caustic taste. It has a density of 8.5, being a little more than half as heavy as air. The gas is liquefied by passing into a tube cooled to —40° by means of a mixture of ice and calcium chloride. It may also be liquefied by subjecting to a pressure of from six to seven atmospheres at ordinary temperatures. This liquid is colorless and highly refractive, and may be solidified by cooling to —75°. At —38.5° it boils, and in vaporizing absorbs large quantities of heat. On account of this property it is used in ice machines and in the several varieties of cooling apparatus used in breweries.

Ammonia is very soluble in water, one volume of the latter absorbing 1148 volumes of the gas at 0°, and about 600 volumes at ordinary temperatures. This solution, which is official in two strengths, will be described later.

Ammonia is not a combustible gas, although if it be mixed with a small quantity of oxygen combustion readily takes place on the application of flame, with the formation of water, nitrogen, and nitric acid. Ammonia is alkaline to litmus paper, and combines with acids, forming the well-known ammonium salts. The formula NH_4 represents a hypothetical compound which has many properties in common with those of sodium and potassium, and will be treated of in connection with them.

Uses.—Anhydrous liquid ammonia is prepared on a large scale for use in ice machines. It comes in commerce in large iron drums strong enough to withstand the pressure necessary to keep it in the liquid condition. The aqueous solution of ammonia is used largely in medicine and in the manufacture of pharmaceutical preparations.

Detection.—Ammonia and its solution are easily detected by the odor; in smaller quantities by bringing over the suspected solution a piece of moistened red litmus paper, which will be turned blue. Still more delicate is the reaction with fumes of hydrochloric acid. A rod moistened with the diluted acid is brought into some of the gas or over some of the warm solution, when immediately white fumes of ammonium chloride will form. When combined with acids, ammonia is detected by first liberating it from its combination with an alkali like potassium or sodium hydrate, and then applying one of the above tests for the gas, or the solution is acidified with hydrochloric acid and solution of platinic chloride added, when a yellow precipitate of ammonio-platinic chloride—$(NH_4)_2PtCl_6$—will slowly separate out in minute crystals. Einbrodt's reagent, consisting of a solution of mercuric chloride to which a minute quantity of an alkaline carbonate has been added, will detect the merest trace of ammonia or its compounds, if the latter are previously made alkaline, by forming a white precipitate or cloudiness. Nessler's reagent produces a brown precipitate with ammonium compounds, or if in very dilute solution a brown or yellow color. This reagent is made by adding to a solution of mercuric chloride a solution of potassium iodide until the precipitate at first formed is nearly all redissolved. Solution of potassium hydrate is then added to strongly alkaline reaction and the liquid allowed to settle until it becomes clear, when it is decanted from any sediment.

Aqua Ammoniæ, U. S. P.—The solution of ammonia is official in two strengths, one, *aqua ammoniæ*, containing 10 per cent, by weight, of the gas, and the other, *aqua ammoniæ for-*

tior, containing 28 per cent., by weight, of the gas. That of 10 per cent. strength has the specific gravity 0.960 at 15°, and the stronger solution has the specific gravity 0.901 at 15°. The commercial "F. F. F." or "20°" water of ammonia contains about 14 per cent. of the gas.

The commercial solution of ammonia is sometimes prepared by the addition of milk of lime to gas liquor and passing the resulting gas into water, but it is difficult to purify such gas from empyreumatic products. This is accomplished in great part by passing the gas through a number of wash-bottles, and then through a series of tubes containing charcoal.

The solution is usually made, however, especially for medicinal purposes, by heating ammonium chloride or sulphate with milk of lime:

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2NH_3 + 2H_2O.$$

The gas is first passed through a little water to wash it, and then into a series of vessels filled with water, in which it is absorbed. The vessel nearest the generator becomes saturated first and is removed, the others are moved up to take its place, and a vessel of fresh water is attached at the end.

Properties.—Solution of ammonia is a colorless, transparent liquid with the pungent alkaline odor and taste of the gas. On the application of heat the solution evolves ammonia gas at a temperature considerably below the boiling point of water. The gas may also be removed by passing air into the solution. In this case there is a great absorption of heat by the escaping gas. With the stronger solution it is said that a temperature of —40° may be attained and a small quantity of mercury frozen.

Spiritus Ammoniæ, U. S. P.—This is an alcoholic solution of ammonia containing 10 per cent., by weight, of the gas. The gas is recommended to be prepared by heating the stronger aqueous solution, and the alcohol is directed to be recently distilled. It would probably be better to distil the alcohol from a little sodium hydrate, and then the darkening which it is intended to avoid would not occur. The specific gravity of the alcoholic solution is about 0.810 at 15.°

Impurities and Tests.—The same tests for purity apply to all the official solutions of ammonia. All should volatilize without residue. No empyreumatic odor should be developed on supersaturating some of the solution with sulphuric acid. All the olutions should remain clear on mixing with five volumes of ime water, indicating the absence of carbonates. Hydrochloric acid when present may be detected by supersaturating with nitric acid and adding silver nitrate.

Sulphuric acid may be detected by similarly saturating with nitric acid and adding solution of barium chloride. Metallic impurities may be detected by the addition of hydrogen sulphide, and calcium salts by the addition of ammonium oxalate.

PRACTICAL EXERCISES.

(1) In a test-tube or evaporating dish mix equal quantities of powdered calcium oxide (quicklime) and ammonium chloride, with a few drops of water; the odor of ammonia will be immediately developed. In smaller quantities the gas may be recognized by holding over the mixture a strip of moistened red litmus paper, which will become blue.

(2) Prepare a larger quantity of the gas by heating in an ordinary flask some ammonia water; at comparatively low temperatures the gas is evolved freely. If it be desired to dry the gas it is accomplished by passing it over quicklime.

Ammonia is collected by *upward displacement;* that is, by passing the delivery-tube upward into a test-tube or jar inverted over it. The gas being lighter than air rises and displaces the latter.

(3) Place a vessel filled with ammonia gas, mouth downward, into some water and agitate slightly; the water will rise in the vessel rapidly, nearly filling it, showing the great solubility of the gas in water.

(4) On applying a lighted taper to the gas the latter does not burn; if, however, it be mixed with oxygen it will ignite readily. A lighted taper is extinguished when plunged into the gas.

DIAMINE, N_2H_4.

HYDRAZINE.

This compound was discovered in 1887, and is obtained when certain nitrogenous organic compounds are decomposed. In many respects it resembles ammonia, being a colorless gas, with a peculiar ammoniacal odor and a strong alkaline reaction. It is very soluble in water, forming a hydrate of the formula $N_2H_4.H_2O$. This combines with acids like ammonia, but with twice the combining power, the formula of the sulphate being $N_2H_4H_2SO_4$, and the chloride $N_2H_4(HCl)_2$.

HYDROXYLAMINE, NH_2OH.

This compound is prepared by the action of nascent hydrogen on some oxygen compound of nitrogen, for example, nitric acid:

$$HNO_3 + 3H_2 = NH_2OH + 2H_2O.$$

Like ammonia and hydrazine, it is soluble in water. This solution, which is the only form in which it is known, is a colorless, odorless, alkaline, and strongly reducing liquid, which precipitates the metals gold, mercury, and silver from solutions of their salts.

On the application of heat to the solution partial decomposition takes place, ammonia, hydroxylamine, and water distilling.

Hydroxylamine unites with acids, the chloride having the formula $NH_2OH.HCl$, or NH_4OCl.

NITROGEN AND CHLORINE.

NITROGEN CHLORIDE, NCl_3.

Preparation.—It is prepared by acting on ammonium chloride with chlorine:

$$NH_4Cl + 3Cl_2 = NCl_3 + 4HCl.$$

It is also formed when solution of ammonium chloride is submitted to the electric current; the chlorine which forms at the positive pole acts on the ammonium chloride. In order to obtain the pure product, the oil which separates in one of the above methods is well washed with cold water to remove ammonium chloride and then dried in a current of chlorine.

Properties.—Nitrogen chloride is a yellow oil of the specific gravity 1.653. It possesses a disagreeable, pungent odor, and the vapor which always escapes on exposure to air attacks the eyes. It is one of the most violent explosives known. The explosion takes place on the slightest provocation, as exposure to sunlight or contact with many kinds of organic matter, as caoutchouc or turpentine.

NITROGEN IODIDE, NI_3.

Preparation.—It is prepared by powdering a little iodine in a mortar and covering with solution of ammonia; after standing ten minutes the insoluble portion is collected on a filter.

Properties.—While moist, nitrogen iodide is comparatively safe in small quantities, but so soon as it becomes dry it explodes on the slightest touch. It is a black powder, and is variously stated by different authors to have the composition NI_3 or NHI_2. It is probable that the substance obtained as above described is a mixture of two or more compounds.

NITROGEN FLUORIDE, NF_3.

This is prepared, like nitrogen chloride, by the electrolysis of ammonium fluoride. It is a highly explosive compound.

NITROGEN AND OXYGEN.

Nitrogen combines with oxygen in five different proportions, three of which form acids, as follows:

Oxides.	Acids.
Nitrogen monoxide, N_2O.	Hyponitrous acid, HNO.
Nitrogen dioxide, N_2O_2.	
Nitrogen trioxide, N_2O_3.	Nitrous acid, HNO_2.
Nitrogen tetroxide, N_2O_4.	
Nitrogen pentoxide, N_2O_5.	Nitric acid, HNO_3.

NITROGEN MONOXIDE.

Formula, N_2O. *Molecular Weight*, 43.98.

History.—Nitrogen monoxide, which is also known by the names nitrous oxide and laughing gas, was discovered by Priestley in 1772.

Preparation.—This gas is formed when zinc is dissolved in diluted nitric acid:

$$\underset{\text{Zinc.}}{4Zn} + \underset{\substack{\text{Nitric}\\\text{Acid.}}}{10HNO_3} = \underset{\substack{\text{Zinc}\\\text{Nitrate.}}}{4Zn(NO_3)_2} + \underset{\substack{\text{Nitrogen}\\\text{Monoxide.}}}{N_2O} + \underset{\text{Water.}}{5H_2O.}$$

The usual method of preparing the gas is by heating ammonium nitrate to 200°, when it is decomposed into water and nitrogen monoxide.

$$\underset{\substack{\text{Ammonium}\\\text{Nitrate.}}}{NH_4NO_3} = \underset{\substack{\text{Nitrogen}\\\text{Monoxide.}}}{N_2O} + \underset{\text{Water.}}{2H_2O.}$$

The most probable impurity in ammonium nitrate is ammonium chloride, which would occasion the presence of chlorine in the gas. It is, therefore, best to pass the gas through three wash-bottles, one of ferrous sulphate solution to remove the other oxides of nitrogen, one of sodium hydrate solution to remove chlorine, and, finally, one of pure water. Since one volume of water absorbs three-fourths of a volume of nitrogen monoxide, a larger yield is obtained by warming the water over which it is collected. On the large scale it is customary to use iron retorts, and after passing the gas through the washings above mentioned to run it into large gasometers over water, taking care to keep the same water in constant use, as after the latter is once saturated there is comparatively little loss.

Properties.—Nitrogen monoxide is a colorless gas of a faint, peculiar odor and a sweetish taste. It is twenty-two times heavier than hydrogen. Under ordinary atmospheric pressure it liquefies at —88°, and at —100° becomes solid. It may also be liquefied at 0° by a pressure of thirty atmospheres. Liquid nitrogen monoxide is colorless and very mobile, and has a specific gravity of 0.9369 at 0°. A drop of the liquid, when brought in contact with the skin, will cause a blister, and water poured on the liquid is immediately frozen, producing at the same time an explosive evolution of the gas. Carbon disulphide dissolves the liquid, and on bringing the mixture under the receiver of an air-pump and exhausting, the temperature of the solution may be reduced to —140°.

Gaseous nitrogen monoxide supports the combustion of ma substances almost as actively as oxygen.

Uses.—The gas is extensively used by inhalation in mi surgery and dentistry, where a short anæsthetic effect is desi For this purpose the gas must be perfectly pure. One of greatest safeguards is to have pure ammonium nitrate from wh to make it. When mixed with air or oxygen the gas produ a condition of partial insensibility, in which the patient of becomes hysterical, laughing immoderately, hence the na *laughing gas.*

It is manufactured on a large scale, and pumped into str steel cylinders under a pressure of sixty-five atmospheres, and a temperature of 5° to 10°. There are two sizes of these cy ders, one containing one hundred gallons, and the other f hundred and fifty to five hundred gallons of the gas. The c tents of the small cylinders weigh about one and a half poun that of the large cylinders about seven pounds. The gas is dra into rubber bags before administering, as a low temperatur caused by its release from pressure. A solution of the gas, un the name of "nitrous oxide water," is made by forcing it i water under a pressure of five atmospheres. This solution is puted to have some medicinal value.

PRACTICAL EXERCISES.

(1) Heat a small quantity of ammonium nitrate in a test-tube, which is attached a delivery-tube, as in the preparation of oxygen. T gas is nitrogen monoxide and may be collected over water.

(2) Plunge a lighted taper into the gas; it is not combustible, bu increases the energy of the combustion of the taper; it is, therefore, a combustible gas, but it supports combustion with an energy alm equal in many cases to that of oxygen.

HYPONITROUS ACID.

Formula, HNO. *Molecular Weight*, 30.97.

This acid is known only in dilute solution or in combination with cert bases. When an aqueous solution of potassium nitrate is treated w sodium amalgam in the proportion of four atoms of sodium to one m cule of the nitrate, potassium hyponitrite is formed:

$$KNO_3 + 2H_2 = KNO + 2H_2O.$$

On carefully neutralizing with acetic acid, and adding silver nitrat yellow precipitate of silver hyponitrite, AgNO, separates. From researches on a volatile compound of hyponitrous acid, it is probable t the formula is $H_2N_2O_2$, or double that above given. This is rende more evident by the fact that some of the acid salts have been prepar which would require the presence of two hydrogen atoms in the molecule. All the salts are quite unstable.

NITRIC OXIDE, OR NITROGEN DIOXIDE.

Formula, NO, *or* N_2O_2. *Molecular Weight*, 59.94.

Preparation.—When nitric acid is added to copper turnings, in a suitable vessel, nitrogen dioxide is evolved:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + N_2O_2 + 4H_2O.$$

Mercury, silver, and some other metals will also give this result. As it comes off at first the gas is of a reddish color, but when the air is all driven out the compound becomes colorless and may then be collected over water. As prepared in this manner the gas is not quite pure, but it may be purified by passing it into a cold, concentrated solution of ferrous sulphate, which absorbs it, and afterward, when heated, gives it off pure. Nitrogen dioxide may more readily be obtained pure by acting on ferrous sulphate with potassium nitrate and sulphuric acid:

$$\underset{\text{Ferrous Sulphate.}}{6FeSO_4} + \underset{\text{Potassium Nitrate.}}{2KNO_3} + \underset{\text{Sulphuric Acid.}}{5H_2SO_4} = \underset{\text{Ferric Sulphate.}}{3Fe_2(SO_4)_3} + \underset{\text{Acid Potassium Sulphate.}}{2KHSO_4} + \underset{\text{Water.}}{4H_2O} + \underset{\text{Nitrogen Dioxide.}}{N_2O_2}.$$

The proportions for the above reaction are 30 grammes of potassium nitrate, 240 grammes of ferrous sulphate, and 250 c.c. of a mixture of one volume concentrated sulphuric acid and three volumes of water.

Properties.—Nitrogen dioxide is a colorless gas. It is not liquefied by a temperature of —110° or a pressure of fifty atmospheres. It combines with the oxygen of the air, forming red fumes of the tetroxide. It is not a combustible gas nor does it support ordinary combustion. Phosphorus when melted will not ignite in it, but if previously ignited it will burn with great brilliancy. A mixture of nitrogen dioxide and carbon disulphide, when ignited, burns with a blinding, bluish-white flame, which is remarkable for its chemically active rays.

NITROGEN TRIOXIDE.

Formula, N_2O_3. *Molecular Weight*, 75.90.

Preparation.—When nitric acid of specific gravity 1.35 is heated with starch, orange-red fumes are evolved, which consist of a mixture of nitrogen trioxide and tetroxide. On passing these vapors, mixed with nitric oxide, N_2O_2, through a hot tube and then into a vessel surrounded by a freezing mixture, the pure trioxide will be obtained. The mixed vapors, when cooled, form a green liquid; but pure trioxide, at —10°, is an indigo-blue liquid. It does not solidify at —30°, and at 0° the liquid begins to decompose into N_2O_2 and N_2O_4. With a small quantity of water nitrogen trioxide forms nitrous acid:

$$N_2O_3 + H_2O = 2HNO_2.$$

With a large quantity of water decomposition takes place and nitric acid results.

NITROUS ACID.

Formula, HNO_2. *Molecular Weight*, 46.93.

Preparation.—This acid is prepared by adding liquefied nitrogen trioxide to ice water. It is so unstable that it cannot be obtained in a state of purity. It is a blue liquid, which is readily decomposed into nitric acid and nitric oxide.

Nitrites.—The salts of nitrous acid are quite stable compounds, and are usually prepared by carefully heating the nitrates. On account of their solubility in alcohol this substance is used to separate the nitrite from the undecomposed nitrate. The addition of copper or lead is often resorted to in order to facilitate the reduction by combining with the liberated oxygen.

The nitrites are distinguished from the nitrates by giving off reddish fumes on the addition of acids. All the nitrites are soluble in water, and most of them are soluble in alcohol.

NITROGEN TETROXIDE, OR PEROXIDE.

Formula, N_2O_4, *or* NO_2. *Molecular Weight*, 91.86.

Preparation.—This compound is prepared by bringing together two volumes of nitric oxide, NO, and one volume of oxygen. The resulting red gas may be condensed to a liquid, or even to a solid, by passing it into a tube immersed in a freeezing mixture.

Many nitrates on heating give off this gas. Lead nitrate is usually employed:

$$\underset{\substack{\text{Lead}\\\text{Nitrate.}}}{2Pb(NO_3)_2} = \underset{\substack{\text{Lead}\\\text{Oxide.}}}{2PbO} + \underset{\substack{\text{Nitrogen}\\\text{Tetroxide.}}}{2N_2O_4} + \underset{\text{Oxygen.}}{O_2}.$$

The vapors of the tetroxide are separated from the oxygen by passing the two through a freezing mixture, whereby the former is condensed.

When arsenous oxide, As_2O_3, is gently heated in a retort with nitric acid of the specific gravity 1.393, the tetroxide is given off abundantly, and condensed as described above:

As_2O_3	+ $4HNO_3$	= As_2O_5	+ $2N_2O_4$	+ $2H_2O$.
Arsenous Oxide.	Nitric Acid.	Arsenic Oxide.	Nitrogen Tetroxide.	Water.

The small amount of nitrogen trioxide, N_2O_3, which is produced at the same time, may be converted into the tetroxide by passing a slow stream of oxygen into the condensed vapors.

Properties.—Nitrogen tetroxide is a liquid which shows some remarkable changes of color: at —9° it solidifies to a mass of colorless crystals, when liquefied at a little above this temperature it is still free from color, but commences to darken, and when the temperature reaches 0° it is yellow. Above this it gradually shades into a brown, until at 22° it boils, giving off deep, reddish-brown fumes. At a little above the boiling point it has a vapor density nearly represented by the formula N_2O_4, but as the temperature increases the vapor become darker in color, and at 140° the density corresponds to the formula NO_2.

The liquid is very corrosive and a powerful oxidizer, and the fumes are very irritating. With water nitrogen tetroxide decomposes into nitric acid and nitric oxide.

NITROGEN PENTOXIDE.

Formula, N_2O_5. *Molecular Weight*, 107.82.

Preparation.—When dry chlorine is passed over dry silver nitrate in a U tube heated to 95°, there is first formed nitrosyl chloride, NO_2Cl, which by further action on the silver nitrate at 60° gives nitrogen pentoxide:

$$AgNO_3 + Cl_2 = NO_2Cl + AgCl + O,$$
$$AgNO_3 + NO_2Cl = N_2O_5 + AgCl.$$

It is also prepared by adding phosphorus pentoxide to anhydrous nitric acid cooled to 0°, and carefully distilling the mixture in a retort attached to a well-cooled receiver:

$$2HNO_3 + P_2O_5 = N_2O_5 + 2HPO_3.$$

The products are nitrogen pentoxide and metaphosphoric acid.

Properties.—Nitrogen pentoxide is a white, colorless, crystalline solid. The crystals melt at 29.5° to a dark-yellow liquid, which boils with decomposition at 45° into nitrogen tetroxide and oxygen.

When heat is applied suddenly this decomposition takes place with explosive violence. It dissolves in water with evolution of heat and forms nitric acid:

$$N_2O_5 + H_2O = 2HNO_3.$$

When brought in contact with many substances, as phosphorus and sulphur, it oxidizes them, the former with ignition; organic matter is also violently attacked.

Nitrogen pentoxide combines with nitric acid to form pernitric acid, having the formula $N_2O_5.2HNO_3$. This is a liquid at ordinary temperatures, having the specific gravity 1.642 at 18°, but is crystalline at 5°. It corresponds to disulphuric acid.

NITRIC ACID

Formula, HNO_3. *Molecular Weight*, 62.89.

History.—Nitric acid was prepared by Geber, in the eighth century, by the distillation of saltpetre with alum or copper sulphate. The composition of the acid was first made known through the investigations of Lavoisier, in 1776, and Cavendish, in 1784.

Occurrence and Formation.—Nitric acid is not found in the free state in nature, but in combination with potassium, sodium, calcium, magnesium, and ammonium it is widely distributed. In warm countries these salts occur as an efflorescence on the surface of the ground and walls where organic matter is decaying. The largest known deposits are the nitrate of soda beds in the provinces of Tarapaca and Atacama, rainless districts on the Peruvian coast. The origin of these great deposits is a matter of conjecture, but it has been suggested that they are the result of the decomposition of sea plants and animals deposited by the receding ocean.

The production of potassium nitrate is carried out artificially in the nitre plantations of India. This was formerly the chief source of the world's supply of potassium salt or saltpetre. Animal matter is mixed with lime and ashes, and the mass exposed to the air but sheltered from the rain. The pile is kept moistened with urine for three years, when it is lixiviated with water. A cubic meter is said to yield twenty kilos. of nitre.

Nitric acid is formed when hydrogen is burned in oxygen containing a small quantity of nitrogen.

When air in a glass globe is submitted to a series of electric sparks, red fumes of nitrogen tetroxide are formed, which in the presence of water are decomposed with the formation of nitric acid. When the air is compressed the production of red fumes is increased.

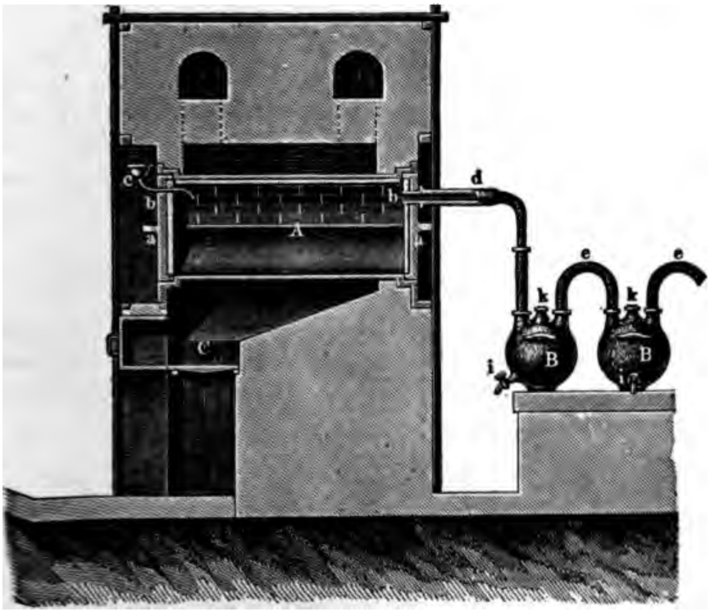
Preparation.—On the small scale nitric acid is prepared by heating in a glass retort equal parts of potassium nitrate and sulphuric acid:

$$\underset{\substack{\text{Potassium}\\\text{Nitrate.}}}{KNO_3} + \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{H_2SO_4} = \underset{\substack{\text{Acid Potassium}\\\text{Sulphate.}}}{KHSO_4} + \underset{\substack{\text{Nitric}\\\text{Acid.}}}{HNO_3}.$$

The apparatus becomes filled with reddish-brown vapors, and the liquid which condenses has a yellowish color on account of the presence of nitrogen tetroxide. The absolute acid is prepared by placing the above distillate with 2 volumes of concentrated sulphuric acid in a retort connected with a well-cooled receiver, and applying a gentle heat. The distillate in this case is freed from color by warming gently and passing through it a current of air to remove the fumes of the lower oxides of nitrogen. The acid can in this way be made to contain about 99.5 per cent. of HNO_3.

On the large scale, in an apparatus similar to that shown in Fig. 55, 700 parts of sodium nitrate or Chili saltpetre are heated in a cast-iron retort, A, with 600 parts of sulphuric acid of the specific gravity 1.84, and the retort connected with 25 receivers,

FIG. 55.



Preparation of nitric acid.

B, B, which contain such a quantity of water as will make the acid of the specific gravity 1.35 to 1.42. The product in this case contains chlorine and iodic acid, and is purified by distilling from glass retorts. The chlorine passes over first, then the receivers are changed, when the pure acid comes over until only a small residue is left in the retort; this residue contains iodic acid, sulphuric acid, and sodium sulphate. Half the quantity of sulphuric acid may be used in the above processes, when neutral sodium sulphate will remain in the retort:

$$\begin{array}{ccccccc} 2NaNO_3 & + & H_2SO_4 & = & Na_2SO_4 & + & 2HNO_3. \\ \text{Sodium Nitrate.} & & \text{Sulphuric Acid.} & & \text{Sodium Sulphate.} & & \text{Nitric Acid.} \end{array}$$

While this is more economical of original material, the higher heat necessary causes a greater decomposition of nitric acid and a more destructive action on the retort. The resulting sodium or potassium sulphate is more difficult to remove, as it remains as a hard, solid mass, while the acid sulphate is in a liquid condition at a moderate temperature and may be poured out.

Properties.—Nitric acid is a colorless, fuming, very corrosive liquid. When absolute, it has a specific gravity of 1.530, and commences to boil at 86°, but on account of partial decomposition into water, nitrogen tetroxide, and oxygen, the temperature rises, until at 120.5° a liquid containing 68 per cent. of the acid distils over unchanged, and has a specific gravity of 1.414 at 15°. When a weaker acid is heated, water is first given off until the acid attains the strength of the above, when it distils unchanged. **Acidum Nitricum,** U. S. P., has a specific gravity of 1.42, and contains 69.4 per cent. of absolute nitric acid, and closely corresponds to the commercial nitric acid.

Nitric acid is a powerful oxidizing agent. It first oxidizes most of the metals and then dissolves them, forming nitrates. Sulphur, phosphorus, and carbon are oxidized by it to oxides or acids. Many organic bodies, like turpentine, are inflamed at once on coming in contact with it, while other organic compounds are merely turned yellow. A number of substances, like cotton and benzene, undergo a process of *nitration* when brought in contact with the concentrated acid. In this operation the group NO_2 replaces hydrogen in the compound. With cotton or cellulose, gun cotton (cellulose nitrate) is formed, with glycerin, nitroglycerin (glyceryl nitrate), and with benzene, nitrobenzene.

The red *fuming* nitric acid differs from the ordinary variety b containing the oxides of nitrogen in solution. It is usually p pared by the method mentioned above, in which a quantity of sulphuric acid is used sufficient to decompose the nitre with formation of neutral sodium sulphate. The high heat necessary to carry out this process decomposes a part of the nitric acid with the formation of red fumes.

Detection.—Nitric acid is easily detected by its action on copper, which it dissolves with a blue color, giving off abundant brown-red fumes at the same time. When wool and silk are brought in contact with strong nitric acid they are colored yellow, and the color is not discharged by ammonia. The acid destroys the blue color of indigo solution, forms a dark ring when brought in contact with a crystal of ferrous sulphate and sulphuric acid, is colored red by brucine, and gives off ammonia when made strongly alkaline with potassium hydrate and heated with zinc.

Impurities and Tests.—Mineral impurities are detected by evaporating to dryness, when no residue should remain. The absence of hydrochloric acid is determined by silver nitrate, and the freedom from sulphuric acid by barium chloride. On diluting with water and adding a small quantity of solution of starch, no blue color should be produced, thus showing the absence of iodine. Iodic acid may be detected with this test by first adding some hydrogen sulphide.

Nitrates.—Nitric acid is monobasic and forms with bases, by replacement of its one hydrogen atom, a series of salts known as nitrates. The most of them are prepared by dissolving the metal in the acid. In the case of the alkalies and alkaline earths, the carbonate, oxide, or hydrate is used to neutralize the acid.

The nitrates are nearly all soluble in water, the exceptions being a few of the basic salts which this acid forms. On the application of heat they evolve, first oxygen and then nitrogen tetroxide, or a mixture of nitrogen and oxygen, leaving an oxide of the metal.

PRACTICAL EXERCISES.

Place a small quantity of potassium nitrate in a test-tube, add sulphuric acid, and apply a gentle heat; brown, strongly acid fumes will be given off. Dilute with water and add indigo solution; the latter loses its blue color, becoming yellow or brown. This is a characteristic test for nitric acid.

Acidum Nitrohydrochloricum, U. S. P.—This substance, which is also known by the names aqua regia and nitromuriatic acid, was first prepared by Geber, who dissolved ammonium chloride in nitric acid. Basil Valentine appears to have given it the name *aqua regia*, and suggested the method for preparing it, used at the present time, by mixing nitric and hydrochloric acids.

Preparation.—The U. S. P. recommends the preparation of it by mixing 18 parts of nitric with 82 parts of hydrochloric acid, all by volume. They should be mixed in an open vessel, allowed to stand until effervescence has ceased, and preserved in partly filled bottles in a cool place. The compounds formed by the combination of the two acids are chlorine and nitrosyl chloride:

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$

Properties. — Nitrohydrochloric acid is a "golden-yellow, fuming, very corrosive liquid, having a strong odor of chlorine" and a strongly acid reaction. It is wholly volatilized on the application of heat, and readily dissolves gold and platinum. This solvent action depends largely on the chlorine which is present.

Nitroxyl chloride, NO_2Cl, is formed when a mixture of nitrogen tetroxide and chlorine is passed through a heated glass tube, and, as has already been shown, it is produced in the action of chlorine on silver nitrate. It is usually prepared, however, by heating lead nitrate with phosphorus oxychloride:

$$\underset{\substack{\text{Phosphorus}\\ \text{Oxychloride.}}}{2POCl_3} + \underset{\substack{\text{Lead}\\ \text{Nitrate.}}}{3Pb(NO_3)_2} = \underset{\substack{\text{Lead}\\ \text{Phosphate.}}}{Pb_32PO_4} + \underset{\substack{\text{Nitroxyl}\\ \text{Chloride.}}}{6NO_2Cl.}$$

Nitroxyl chloride is a heavy, oily, yellow liquid which boils at 5°, and is readily decomposed by water into nitric and hydrochloric acids.

Nitrosyl chloride, NOCl, is formed by the union of nitrogen dioxide and chlorine:

$$N_2O_2 + Cl_2 = 2NOCl.$$

It is also produced by the action of phosphorus pentachloride on potassium nitrite:

$$PCl_5 + KNO_2 = NOCl + KCl + POCl_3.$$

Being one of the products obtained on mixing nitric and hydrochloric acids, it exists in "aqua regia."

It is an orange-yellow gas, and in a freezing mixture condenses to a liquid, which fumes strongly and possesses the odor of "aqua regia." It combines with mercury, forming mercurous chloride, and liberating nitrogen dioxide; neither gold nor platinum is dissolved by it.

Nitrosyl bromide, NOBr, is prepared by leading nitrogen dioxide into bromine at a temperature of —10° to —15° as long as it is absorbed. A blackish-brown liquid results, which decomposes at —2°, giving off nitrogen dioxide, and leaving nitrosyl tribromide, $NOBr_3$, a dark, brownish-red liquid.

Nitrogen sulphide, N_2S_2, is obtained in an impure condition by the action of dry ammonia on sulphur chloride or thionyl chloride. It is yellow crystalline powder, soluble in carbon disulphide. When heated to 135°, it sublimes, depositing yellowish-red crystals. It melts at 158° with decomposition.

There exists a similar compound of nitrogen and selenium, N_2Se_2.

PHOSPHORUS.

Symbol, P. *Atomic Weight*, 30.96. *Valence*, III.

History.—Phosphorus was discovered by the alchemist Brandt, in 1669, at Hamburg. He prepared it by distilling a mixture of evaporated urine and sand. A hundred years later it was shown by Gahn to be a constituent of bones, and in 1771 Scheele published a method for preparing it from this source.

Occurrence.—Phosphorus is never found native in the free state, but chiefly as calcium phosphate, the principal constituent of bones, as well as of the minerals *apatite* and *phosphorite*. Very extensive deposits of calcium phosphate are found near Charleston, South Carolina, in Florida, and in several other of the Southern States. This "phosphate rock," as it is called, contains also some iron, alumina, carbonic acid, and fluorine. It is collected and shipped in enormous quantities to many parts of the world to be used for fertilizing purposes.

Phosphorus is, further, very widely distributed in comparatively small quantities. It is always found in plant and animal tissues, in the soil, and in sea water. The source of the element is largely bones, although a portion of that made in England is prepared from *sombrerite*, a mineral from the island of Sombrero in the West Indies, consisting of impure calcium phosphate.

Preparation.—The bones are freed from fat by carbon disulphide or petroleum benzin, and from gelatin by superheated steam. They are then burned to whiteness. The resulting white boneash is composed of 86 per cent. calcium phosphate, $Ca_3(PO_4)_2$, and small quantities of magnesium phosphate and calcium carbonate and fluoride.

This boneash or its equivalent, the calcined spent boneblack from the sugar refiners, or *sombrerite*, is treated with an equal weight of 50 per cent. sulphuric acid:

$$\underset{\text{Calcium Phosphate.}}{Ca_3(PO_4)_2} + \underset{\text{Sulphuric Acid.}}{2H_2SO_4} = \underset{\text{Acid Calcium Phosphate.}}{CaH_4(PO_4)_2} + \underset{\text{Calcium Sulphate.}}{2CaSO_4}.$$

The solution of acid phosphate is decanted from the calcium sulphate, evaporated to dryness, and heated to redness, by which it loses water and is converted into calcium metaphosphate:

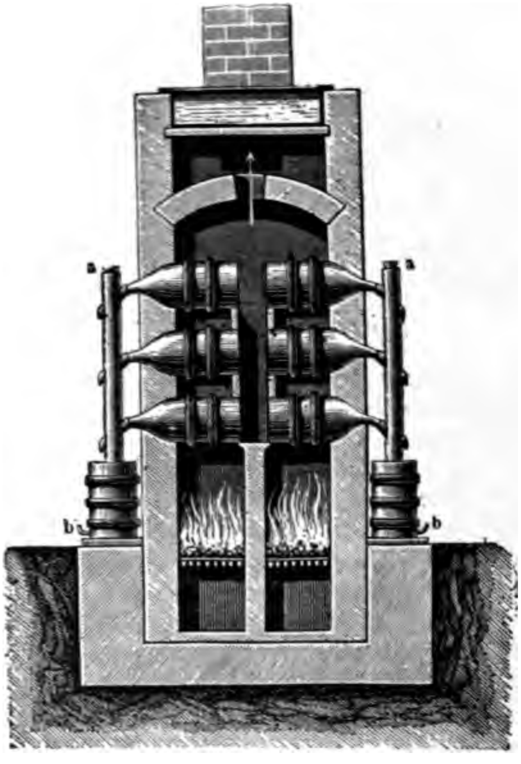
$$\underset{\substack{\text{Acid Calcium}\\\text{Phosphate.}}}{CaH_4(PO_4)_2} = \underset{\substack{\text{Calcium}\\\text{Metaphosphate.}}}{Ca(PO_3)_2} + \underset{\text{Water.}}{2H_2O.}$$

The calcium metaphosphate is very intimately mixed with charcoal, and gradually heated in earthenware retorts to a white heat, when the following reaction takes place:

$$\underset{\substack{\text{Calcium}\\\text{Metaphosphate.}}}{3Ca(PO_3)_2} + \underset{\text{Charcoal.}}{10C} = \underset{\text{Phosphorus.}}{P_4} + \underset{\substack{\text{Calcium}\\\text{Phosphate.}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{Carbon}\\\text{Monoxide.}}}{10CO.}$$

The yield amounts to two-thirds of the phosphorus which is present. The whole of the phosphorus may be recovered by adding enough sand to convert the calcium into silicate, according to the following reaction:

FIG. 56.



Preparation of phosphorus.

$$\underset{\substack{\text{Calcium}\\\text{Metaphosphate.}}}{2Ca(PO_3)_2} + \underset{\text{Silica.}}{2SiO_2} + \underset{\text{Charcoal.}}{10C} = \underset{\substack{\text{Phos-}\\\text{phorus.}}}{P_4} + \underset{\substack{\text{Calcium}\\\text{Silicate.}}}{2CaSiO_3} + \underset{\substack{\text{Carbon}\\\text{Monoxide.}}}{10CO.}$$

The furnace and retorts used in the above distillation are shown in Fig. 56. The yield is from 8 to 10 per cent. of the bones used. Phosphorus at this stage still contains impurities carried over mechanically in the process of distillation, and from these it must be further purified. This is accomplished by redistilling from iron retorts, by pressing through chamois leather under water, or by treating the melted phosphorus under water with a mixture of sulphuric acid and potassium dichromate, three and a half parts of each of these compounds being used for every one hundred parts of the element.

After the purification process the molten phosphorus is run into glass or copper to solidify in the form of sticks, and, after cutting under water, is preserved under the same liquid in barrels, or, better, in sealed tin cans.

Most of the world's supply of this element comes from two manufactories, one at Oldbury, England, and one at Lyons, France. Smaller quantities are produced in Russia, Sweden, and the United States. The present output amounts to about two thousand five hundred tons annually.

Properties.—Like many of the other elements, phosphorus exists in several allotropic forms. That obtained by the above methods is known as *ordinary* or *octohedral* phosphorus.

This variety is a colorless, transparent to translucent, wax-like solid. At ordinary temperatures it is sufficiently soft to be cut by a knife, but at lower temperatures it becomes more brittle. It has a specific gravity of 1.83 at 10°, and at 44° it melts to a colorless liquid. It boils at 290°, air, of course, being excluded. Between the temperatures of 500° and 1000° the vapor of phosphorus has a density of 62, indicating a formula for the molecule of P_4. At a higher temperature it is less, indicating that the molecule under these conditions is made up of a less number of atoms.

Phosphorus is insoluble in water, soluble in 350 parts of absolute alcohol at 15°, and in 240 parts of boiling absolute alcohol, in 80 parts of absolute ether, and in about 50 parts of any fatty oil. Chloroform and benzene dissolve it in considerable quantity, and carbon disulphide is probably its best solvent, dissolving from 18 to 20 times its weight without losing its fluidity. All solutions of phosphorus in carbon disulphide should be preserved with the greatest care. When spilled or otherwise exposed the solvent rapidly evaporates, leaving the phosphorus in such a finely divided condition that it inflames spontaneously. Phosphorus may be powdered by melting under water and agitating until cold; many saline solutions facilitate this division. When exposed to a damp air at ordinary temperatures, phosphorus undergoes slow oxidation, giving off garlic-smelling fumes of phosphorus and phosphoric acids, which are luminous in the dark. It is a very inflammable element, igniting in the air spontaneously at 50°. For this reason it is kept and cut under water. The sticks of phosphorus which are kept under water, exposed to the light, become covered with a white, opaque film, which slowly turns red and peels off. This is due to slight oxidation, and may be prevented by excluding light, and using for covering a pure water that has been recently boiled to remove oxygen and cooled. In pure oxygen phosphorus is not luminous below 15°, but becomes so immediately on the introduction of an inert gas like nitrogen, or by rarefying the oxygen.

Phosphorus combines directly with many elements, like sulphur, chlorine, bromine, iodine, and, at higher temperatures, with many of the metals. With hydrogen and nitrogen it does not combine directly. On account of its affinity for oxygen, it reduces many metallic salts when placed in their aqueous solutions, precipitating the metal. Nitric acid oxidizes phosphorus to phosphoric acid, and solutions of the alkaline hydrates convert it, on boiling, into hypophosphite of the base with evolution of hydrogen phosphide.

Red or *amorphous* phosphorus is an allotropic modification discovered by Schrötter in 1845. It is prepared by heating the ordinary variety in a nearly closed iron vessel to 240° or 250°, or more quickly by having the vessel closed tightly and heating to 300° under pressure, when the conversion takes place in a few moments. It is necessary to introduce an inert gas like nitrogen before heating the phosphorus. At 260°, in an open vessel, the amorphous variety is reconverted into ordinary phosphorus, with evolution of considerable heat. Amorphous phosphorus, prepared as above described, contains some of the ordinary variety, from which it is freed by treatment with carbon disulphide, which leaves the red variety in a state of purity. When purified, amorphous phosphorus has a specific gravity of 2.15. It is not affected by solvents and does not inflame in air until the temperature reaches 260°. A slow oxidation to phosphoric acid takes place at ordinary temperatures.

Amorphous phosphorus is said not to be poisonous, while the ordinary variety is very energetic in its action on the human system. The poisonous results obtained from the former are probably due to the presence of the latter as an impurity.

A third variety, known as *rhombohedral* or *metallic* phosphorus, is obtained by heating the ordinary variety in sealed tubes with metallic lead for ten hours, at a little below a red heat. After cooling, the lead is dissolved in diluted nitric acid, which leaves a mass of dark-red crystals. This modification has a specific gravity of 2.34 at 15°, and requires a temperature of 358° to convert it into the ordinary form. This variety is also obtained when the amorphous phosphorus is heated in a sealed tube to 580°.

Uses.—Phosphorus is used in medicine and in the manufacture of many chemical compounds, frequently without being a constituent of the product, for example, in the preparation of methyl and ethyl iodides. Its most extensive use, however, is in the manufacture of matches and as a poison for vermin.

In the manufacture of matches, phosphorus is submerged in a warm concentrated solution of glue, and then rapidly stirred to prevent it reaching the surface in a mass and igniting. When it has become uniformly mixed, the other ingredients are added, and the matches, previously tipped with paraffin, are dipped. Many mixtures have been proposed; the following is characteristic: phosphorus, 2 parts; manganese dioxide, 1 part; chalk, 3 parts; lampblack, ⅛ part, and glue, 5 parts. In many of the mixtures potassium chlorate or nitrate is used.

On account of the danger to workmen engaged in the manufacture of matches, not only from the ignition of the phosphorus, but also because of the poisonous character of the fumes, it has been proposed to use amorphous phosphorus in the process. In this country, however, the suggestion has not met with much favor. In Europe the so-called *safety matches* are extensively manufactured and used. In order to ignite them these matches require to be rubbed on a certain material. The matches are tipped with a mixture of potassium chlorate, 32 parts; potassium dichromate, 12 parts; red oxide of lead, 32 parts, and antimony sulphide, 24 parts. The composition on the box is made up of amorphous phosphorus and antimony sulphide. These matches may sometimes be ignited by quickly drawing them over a piece of ground glass or a sheet of smooth white paper.

Impurities.—Phosphorus frequently contains arsenic derived from the sulphuric acid used in its manufacture, and at the same time it may be contaminated with sulphur.

The following U. S. P. test is sufficient to identify these impurities: "Add 3 gm. of Phosphorus to 15 c.c. of nitric acid diluted with 15 c.c. of distilled water in a flask having the capacity of 50 c.c., and digest the mixture at a gentle heat on a water-bath, until the Phosphorus is dissolved. Transfer the solution to a capsule, and evaporate it until no more nitrous vapors are given off, and then dilute the solution to 30 c.c. with distilled water. Heat 20 c.c. of the diluted solution to about 70° for half an hour, passing hydrogen sulphide through it during the half-hour's heating, and then until the liquid has become cold. If the liquid be now allowed to stand at rest during twenty-four hours, not more than a very small quantity of lemon-yellow precipitate should be visible (limit of *arsenic*).

"On adding barium chloride T.S. to the remainder of the liquid, not more than a slight opalescence should be produced (limit of *sulphur*)."

PHOSPHORUS AND HYDROGEN.

Phosphorus combines with hydrogen in three proportions:

PH_3, gaseous hydrogen phosphide,
P_2H_4, liquid hydrogen phosphide,
P_4H_2, solid hydrogen phosphide.

Gaseous hydrogen phosphide is prepared by heating hypophosphorous acid:

$$\underset{\text{Hypophosphorous Acid.}}{2H_3PO_2} = \underset{\text{Phosphoric Acid.}}{H_3PO_4} + \underset{\text{Hydrogen Phosphide.}}{PH_3},$$

and by heating phosphorous acid:

$$\underset{\text{Phosphorous Acid.}}{4H_3PO_3} = \underset{\text{Phosphoric Acid.}}{3H_3PO_4} + \underset{\text{Hydrogen Phosphide.}}{PH_3}.$$

Hydrogen phosphide is also evolved when phosphorus is heated with a solution of potassium hydrate:

$$\underset{\text{Potassium Hydrate.}}{3KOH} + \underset{\text{Phosphorus.}}{P_4} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Potassium Hypophosphite.}}{3KH_2PO_2} + \underset{\text{Hydrogen Phosphide.}}{PH_3}.$$

The last is the usual method of preparing the gas, and it is important to observe certain precautions. The air must first be displaced by a stream of carbon dioxide or illuminating gas. The delivery-tube is then put under the surface of water and heat applied. Some time after boiling commences, the escaping gas, as it comes in contact with air, inflames spontaneously with a slight report, and forms a beautiful ring of white smoke.

The other methods of preparation are: by adding tricalcium diphosphide to water:

Ca_3P_2	$+$	$6H_2O$	$=$	$3Ca(OH)_2$	$+$	$2PH_3$,
Tricalcium Diphosphide.		Water.		Calcium Hydrate.		Hydrogen Phosphide.

and by adding phosphonium iodide to water:

PH_4I	$+$	H_2O	$=$	HI	$+$	H_2O	$+$	PH_3.
Phosphonium Iodide.		Water.		Hydriodic Acid.		Water.		Hydrogen Phosphide.

In order to obtain the gas perfectly pure, it is passed through a tube immersed in a freezing mixture, by which means the liquid hydrogen phosphide is condensed. When prepared from phosphonium iodide none of the liquid compound is formed.

Properties.—Hydrogen phosphide, when pure, is a colorless gas with a disagreeable fishy odor. It inflames when heated to 100°, or by slight concussion, forming metaphosphoric acid.

Hydrogen phosphide is a compound analogous to ammonia, and combines with hydrochloric, hydrobromic, and hydriodic acids, forming phosphonium chloride, PH_4Cl, phosphonium bromide, PH_4Br, and phosphonium iodide, PH_4I.

Liquid hydrogen phosphide, P_2H_4, is formed by passing the gas obtained from phosphorus and potassium hydrate through a freezing mixture, by which the liquid phosphide is condensed. It is also formed by the action of water on calcium phosphide:

Ca_2P_2	$+$	$4H_2O$	$=$	$2Ca(OH)_2$	$+$	P_2H_4.
Dicalcium Diphosphide.		Water.		Calcium Hydrate.		Hydrogen Phosphide.

Properties.—This is a colorless, strongly refracting liquid, which inflames spontaneously in contact with air. On exposure to light without access of air it readily decomposes into gaseous and solid hydrogen phosphide. This substance is analogous to the ammonium compound, *hydrazine*, N_2H_4, but is not so stable.

Solid hydrogen phosphide, P_4H_2, is formed when calcium phosphide is dissolved in warm concentrated hydrochloric acid, with exclusion of air. It is a yellow, odorless, and tasteless powder, which on exposure to air changes to an orange color. When heated to 70° with exclusion of air it is decomposed into phosphorus and hydrogen.

PHOSPHORUS AND THE HALOGENS.

Phosphorus combines with the halogens at ordinary temperatures, in some cases with evolution of heat and light. It forms at least two compounds with each, acting with an equivalence of three or five, according to the amount of the halogen present at the time of combination.

Phosphorus trichloride, PCl_3, is prepared by passing dry chlorine into a retort in which there is amorphous phosphorus; a moderate heat is applied to the retort, and the resulting vapors of phosphorus are conducted into a well-cooled receiver. When the phosphorus is kept in excess the product is nearly pure, but if the chlorine be slightly in excess the distillate will also contain phosphorus pentachloride, which may be removed by redistilling from ordinary phosphorus.

Phosphorus trichloride is a colorless, pungent liquid, boiling at 76° and retaining its liquidity at —115°. Its specific gravity at 0° is 1.613. It fumes in contact with moist air, and is decomposed by water into hydrochloric and phosphorous acids:

$$PCl_3 + 3H_2O = 3HCl + H_3PO_3.$$

Phosphorus pentachloride, PCl_5, is formed by the action of dry chlorine on phosphorus trichloride. This is best accomplished by passing the dry chlorine on the surface of the trichloride by a wide tube, occasionally stirring until the whole solidifies to a crystalline mass. As there is considerable heat developed, the vessel in which the reaction takes place must be kept well cooled.

Phosphorus pentachloride is a yellowish-white, crystalline powder, which fumes strongly on exposure to air, with a very irritating odor. It sublimes at 100° without previously melting; by higher temperatures it is decomposed into phosphorus trichloride and chlorine, the dissociation being complete at 336°. It is decomposed by a small quantity of water into phosphorus oxychloride and hydrochloric acid:

$$PCl_5 + H_2O = POCl_3 + 2HCl.$$

With an excess of water, phosphoric and hydrochloric acids are produced:

$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl.$$

$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl.$$

On account of this affinity for the elements of water, phosphorus pentachloride is a useful laboratory reagent for determining the presence of hydroxyl, especially in organic compounds. For example, the reaction with ethyl alcohol is as follows:

$$C_2H_5.OH + PCl_5 = C_2H_5Cl + POCl_3 + HCl.$$

With acetic acid there is formed acetyl chloride, according to the following reactions:

$$C_2H_3O.OH + PCl_5 = C_2H_3O.Cl + POCl_3 + HCl.$$

With an aldehyde in which the oxygen is united by both its bonds to carbon the following reaction expresses the change:

$$C_6H_5CO.H + PCl_5 = C_6H_5CCl_2.H + POCl_3.$$

Phosphorus tribromide, PBr_3, is prepared like the trichloride, which it closely resembles. It has the specific gravity 2.925 at 0°, and boils at 175°.

Phosphorus pentabromide, PBr_5, resembles the corresponding compound of chlorine in its mode of formation and properties. It is a yellow crystalline solid, which melts below 100° and decomposes into the tribromide and bromine.

A compound of phosphorus with both chlorine and bromine may be formed by bringing together phosphorus trichloride and bromine in the proportion of their molecular weights. The resulting compound is called

PHOSPHOROUS OXIDE.

Formula, P_2O_3. *Molecular Weight*, 109.80.

This compound is prepared by gently heating phosphorus with incomplete access of air. An imperfect combustion takes place with the formation of the trioxide.

It is a white, amorphous powder, of a garlic-like odor. In contact with air it inflames, forming the pentoxide.

PHOSPHOROUS ACID.

Formula, H_3PO_3. *Molecular Weight*, 81.84.

Preparation.—This acid is formed when phosphorus is exposed to moist air; although in this case it is mixed with hypophosphoric and phosphoric acids. It is prepared pure and in large quantity by leading a stream of chlorine into melted phosphorus under water. Phosphorus trichloride is first produced, which is decomposed, as fast as formed, by the water present:

$$PCl_3 \quad + \quad 3H_2O \quad = \quad H_3PO_3 \quad + \quad 3HCl.$$

The solution is evaporated until it attains a temperature of 180°, when a thick fluid mass remains, which, on cooling, solidifies to a mass of crystals, having a melting point of 70.1°. On heating above 180° decomposition takes place, with formation of phosphoric acid and hydrogen phosphide, as follows:

$$4H_3PO_3 \quad = \quad 3H_3PO_4 \quad + \quad PH_3.$$

Phosphorous acid is a powerful reducing agent, precipitating gold, silver, and mercury in the metallic state from solutions of their salts.

Phosphites.—The alkali phosphites are all soluble in water, the others are difficultly soluble. The acid is dibasic, one of the three hydrogen atoms not being replaceable by metal. A number of organic salts of phosphorous acid have been prepared, as triethyl phosphite, $(C_2H_5)_3PO_3$. The phosphites are distinguished from the hypophosphites by the former causing precipitates with barium and calcium hydrates.

HYPOPHOSPHOROUS ACID.

Formula, H_3PO_2. *Molecular Weight*, 65.88.

Preparation.—It is prepared by first making calcium or barium hypophosphite. For pharmaceutical purposes the former of these is preferred, and it is made by boiling phosphorus with calcium hydrate:

$$\underset{\substack{\text{Calcium}\\\text{Hydrate.}}}{3Ca(OH)_2} \quad + \quad \underset{\text{Phosphorus.}}{2P_4} \quad + \quad \underset{\text{Water.}}{6H_2O} \quad = \quad \underset{\substack{\text{Calcium}\\\text{Hypophosphite.}}}{3Ca(H_2PO_2)_2} \quad + \quad \underset{\substack{\text{Hydrogen}\\\text{Phosphide.}}}{2PH_3.}$$

The excess of calcium hydrate is converted into carbonate by carbon dioxide, the solution filtered from the calcium carbonate and a small quantity of phosphate, which is formed at the same time, and the clear filtrate either evaporated for the calcium hypophosphite or decomposed with oxalic acid for the free acid:

$$\underset{\text{Calcium Hypophosphite.}}{Ca(H_2PO_2)_2} + \underset{\text{Oxalic Acid.}}{H_2C_2O_4} = \underset{\text{Hypophosphorous Acid.}}{2H(H_2PO_2)} + \underset{\text{Calcium Oxalate.}}{CaC_2O_4}.$$

When barium hypophosphite is used, sulphuric acid is employed to decompose it.

The calcium oxalate is filtered from the acid and the latter evaporated until it contains 50 per cent. of hypophosphorous acid; in which form it usually comes into the market. The acid may be obtained in the solid form, and nearly absolute, by evaporating carefully at or below 130°, and then placing in a freezing mixture. It melts at 17.4°.

Properties.—When strongly heated hypophosphorous acid is decomposed into orthophosphoric acid and hydrogen phosphide. Solution of hypophosphorous acid decomposes salts of gold, silver, and mercury, with formation of the metal. It is oxidized by chlorine and potassium permanganate.

Acidum Hypophosphorosum Dilutum, U. S. P., contains 10 per cent. by weight of absolute HPH_2O_2.

This acid has a specific gravity of 1.046 at 15°, and the 50 per cent. acid at the same temperature has a specific gravity of 1.406. The latter is found in commerce.

Impurities and Tests.—The most probable impurities in this acid are hydrochloric, sulphuric, phosphoric, and oxalic acids, and calcium hypophosphite. The acids may all be readily detected by their appropriate tests, and the calcium by the addition of oxalic acid.

Hypophosphites.—The salts of this acid are prepared from the calcium or barium salt by double decomposition. They are all soluble in water.

In the dry state they are quite stable, but in solution they readily undergo change. In pharmaceutical preparations they are usually protected by sugar.

Hypophosphoric Acid, H_2PO_3, is formed with phosphoric and phosphorous acids when phosphorus is slowly oxidized in moist air. By evaporating the solution to a syrupy consistence, and adding cold, saturated solution of sodium acetate, the sodium salt having the formula $NaHPO_3.3H_2O$ separates out. The acid gives a white precipitate with silver nitrate which does not blacken on boiling. This serves to distinguish it from phosphorous and hypophosphorous acids.

PHOSPHORUS PENTOXIDE.

Formula, P_2O_5. *Molecular Weight*, 141.72.

Phosphorus pentoxide, or phosphoric oxide, is prepared by burning phosphorus in dry air or oxygen. It is a bulky, white, amorphous powder, which is capable of being sublimed. It has a powerful affinity for water, hissing when thrown into it. Unless it be rigidly excluded from moist air deliquescence rapidly takes place. On account of this affinity for moisture it is much used in the drying of gases.

ORTHOPHOSPHORIC ACID.

Formula, H_3PO_4. *Molecular Weight*, 97.80.

History.—The existence of this acid was first noticed by Marggraf, in 1746, on account of the peculiar yellow precipitate it produced with silver nitrate. Graham, in 1833, first pointed out the difference between the ortho-, pyro-, and meta- acids.

Occurrence.—The free acid is not known in nature, but in combination with calcium it occurs abundantly in bones, in all vegetable and animal tissues, and in minerals. The deposits of impure calcium phosphate in Southeastern United States and the adjacent islands are the most abundant occurrences as well as sources of this acid in combination.

Preparation.—The use for which the phosphoric acid is intended determines the method of manufacture. For many purposes the acid is made from boneash by treatment with sulphuric acid:

$$\underset{\text{Calcium Phosphate.}}{Ca_3(PO_4)_2} + \underset{\text{Sulphuric Acid.}}{3H_2SO_4} = \underset{\text{Phosphoric Acid.}}{2H_3PO_4} + \underset{\text{Calcium Sulphate.}}{3CaSO_4}.$$

The clear liquid is decanted from the calcium sulphate and evaporated to a small bulk, when, after settling, the supernatant liquid is again decanted from the further deposit of calcium sulphate; the temperature is then raised to 300°, and maintained at that point until all sulphuric acid is removed. The acid made in this way is useful in the arts and in the manufacture of phosphates.

The official acid is, or should be, prepared directly from phosphorus, by the action of nitric acid. 16 parts of phosphorus ar heated in a capacious retort with 100 parts of nitric acid (sp. g 1.420), diluted with an equal weight of distilled water. Th retort is connected with a condenser, and heat applied unt the reaction commences. The heat is then carefully regulate to prevent the action becoming too violent, and, if necessar distilled water added. The condensed liquid is returned from time to time until the phosphorus is dissolved:

$$\underset{\text{Phosphorus.}}{3P} + \underset{\substack{\text{Nitric}\\ \text{Acid.}}}{5HNO_3} + \underset{\text{Water.}}{2H_2O} = \underset{\substack{\text{Phosphoric}\\ \text{Acid.}}}{3H_3PO_4} + \underset{\substack{\text{Nitric}\\ \text{Oxide.}}}{5NO.}$$

The solution is evaporated at a temperature not exceeding 190°, until the excess of nitric acid is driven off, and a clear, odorless, syrupy liquid remains. Sufficient distilled water is then added to make the liquid weigh 100 parts.

Phosphorus is sometimes contaminated with arsenic, and this should always be removed by diluting the above with one hundred and fifty parts of distilled water, passing in hydrogen sulphide for one-half hour with the liquid at 70°, then removing the heat and continuing the passage of the gas until cold. The liquid is next set aside for twenty-four hours, after which it is filtered and evaporated to 100 parts.

A more expeditious method than this, which has been found to work well on a large scale, was proposed in 1875 by Markoe. 540 parts of distilled water are placed in a large stoneware jar, and the latter set in water. 90 parts of phosphorus are added, then 1 part of iodine, and the whole agitated or stirred in order to bring the iodine and phosphorus in contact. 6 parts of bromine are next run in from a stoppered funnel, drop by drop, in such a way as to bring each drop in contact with the phosphorus and iodine. As soon as the reaction is complete 540 parts of nitric acid (sp. gr. 1.420) are added, and in warm weather a little more water, in order to prevent the action from becoming too violent. The vessel is then covered with a glass or porcelain plate. No further attention is required for from twelve to twenty-four hours. At the end of this time the phosphorus will be found to have disappeared, and the iodine will usually be found sublimed on the lid of the vessel. From this point the process is carried out exactly as in the official method. When the above directions are rigidly adhered to, the operation is an entirely safe one, but in trying to hasten the action by more concentrated solutions explosions have resulted. It is very important to bring every drop of bromine in contact with the phosphorus in order that the reaction may take place before more is added. The iodine is said to modify the action somewhat, but further than that it has no use, for the small amount of bromine is sufficient to act as a carrier of the oxygen from the nitric acid to the phosphorus.

dicating the absence of nitric acid. No precipitate should be formed, after several hours, by the addition of an equal volume of tincture of ferric chloride, indicating the absence of pyro- and meta-phosphoric acids.

Phosphates.—The salts of this acid usually take the name of phosphates. They are prepared by neutralizing the acid with a hydrate or carbonate. The salts of the alkali metals are soluble in water, the other salts are insoluble in water, but readily soluble in hydrochloric acid. Since the acid is tribasic, there are three classes of salts formed, according as one, two, or three of the hydrogen atoms are replaced by a base. When the acid is neutralized by a carbonate two atoms of hydrogen are replaced.

Detection.—Orthophosphates, as well as the acid, are detected by adding silver nitrate to a neutral solution, when a yellow precipitate forms, consisting of silver phosphate, Ag_3PO_4. This precipitate is soluble in nitric acid and in ammonia. Ammonium molybdate in nitric acid solution causes a yellow precipitate to slowly separate, consisting of ammonium phospho-molybdate, $(NH_4)_3PO_4(MoO_3)_{10}$. In alkaline solutions, magnesia mixture causes a white precipitate of ammonium-magnesium-phosphate, $MgNH_4PO_4.6H_2O$. Phosphoric acid does not coagulate albumen.

PYROPHOSPHORIC ACID.

Formula, $H_4P_2O_7$. *Molecular Weight*, 177.64.

Neither pyrophosphoric acid nor its salts are found in nature.

Preparation.—The acid is prepared by prolonged heating of the orthophosphoric acid to from 200° to 300°, until a portion neutralized with ammonia and treated with silver nitrate yields a pure white precipitate free from yellow color. The sodium orthophosphate, when heated to 240°, is converted into sodium pyrophosphate. By double decomposition between this salt and lead nitrate, lead pyrophosphate is precipitated, which by decomposition with hydrogen sulphide yields the free acid. The acid is also formed when ortho- and meta-phosphoric acids are brought together in molecular proportions in a water-bath.

Properties.—Pyrophosphoric acid exists in the form of crystalline masses. It is easily soluble in water, and in solution it very slowly reverts to the ortho- variety. This may be quickly accomplished by heating.

Pyrophosphates.—The salts of pyrophosphoric acid are called pyrophosphates, and are prepared by heating the orthophosphates to 240°. Two series of salts are formed, those in which two atoms of hydrogen are replaced, and those in which four atoms of hydrogen are replaced by bases.

The pyrophosphates of the alkalies are soluble in water; those of other bases are mostly insoluble in water, but soluble in acids. Solutions of the salts in water remain unchanged, but on boiling with acids or fusing with sodium carbonate they are converted into phosphates.

Detection.—Pyrophosphoric acid and its salts are recognized and distinguished from the other varieties by the white precipitate with silver nitrate, by the absence of a precipitate with ammonium molybdate in the presence of nitric acid, and by the inability of the free acid to coagulate albumen.

METAPHOSPHORIC ACID.

Formula, HPO_3. *Molecular Weight*, 79.84.

This acid is also known as glacial phosphoric acid. It is prepared by heating one of the preceding varieties to redness. It is also produced when phosphorus pentoxide is allowed to slowly melt in cold water.

Properties.—Metaphosphoric acid exists in the form of a white pasty mass. It often contains sodium in the form of sodium metaphosphate, which gives it a more vitreous and transparent appearance. The aqueous solution slowly changes to the ortho- variety, quickly on boiling, and without formation of the intermediate pyro- acid.

Metaphosphates.—The salts of this acid are prepared by heating the ortho- salts to redness. As the acid is monobasic we would naturally expect to obtain but one series of salts, but this acid possesses the property of polymerization to such an extent that at least five different series of salts are formed, as follows: RPO_3, metaphosphate; $R_2P_2O_6$, dimetaphosphate; $R_3P_3O_9$, trimetaphosphate; $R_4P_4O_{12}$, tetrametaphosphate; and $R_6P_6O_{18}$, hexametaphosphate.

Detection.—The free acid and its salts are detected and distinguished from the other varieties by the white precipitate with silver nitrate, by not forming a precipitate with ammonium molybdate in presence of nitric acid, by the free acid coagulating albumen, and by the absence of a precipitate with magnesium sulphate in neutral solution.

PHOSPHORUS WITH OXYGEN AND CHLORINE.

Phosphorus oxychloride, $POCl_3$, is formed by decomposing phosphorus pentachloride with water:

$$PCl_5 + H_2O = POCl_3 + 2HCl.$$

For larger quantities the pentachloride is heated with dry oxalic acid:

$$PCl_5 + H_2C_2O_4 = POCl_3 + 2HCl + CO_2 + CO.$$

Phosphorus oxychloride is a colorless liquid, having the specific gravity 1.711 at 0°. When cooled it solidifies to acicular crystals, which melt at —1.5°. On heating it boils at 107.2°. With water it is decomposed into phosphoric and hydrochloric acids:

$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl.$$

Two other compounds of these elements are known: Pyrophosphoryl chloride, $P_2O_3Cl_4$, a colorless, strongly fuming liquid, boiling between 210° and 215°; and metaphosphoryl chloride, PO_2Cl, a thick, syrupy mass, prepared by heating phosphorus pentoxide and oxychloride to 200°.

PHOSPHORUS WITH OXYGEN AND BROMINE.

Phosphorus oxybromide, $POBr_3$. This compound is analogous to the oxychloride, $POCl_3$, and is similarly prepared, by acting on phosphorus pentabromide with the required amount of water:

$$PBr_5 + H_2O = POBr_3 + 2HBr,$$

or by distilling the pentabromide with oxalic acid:

$$PBr_5 + H_2C_2O_4 = POBr_3 + 2HBr + CO_2 + CO.$$

CHAPTER VI.

BORON.

Symbol, B. *Atomic Weight*, 10.9. *Valence*, III.

History.—The element boron was isolated by Gay Lussac and Thénard in 1808, and about the same time independently by Davy. It was known in combination as borax by Geber and the alchemists.

Occurrence.—Boron does not exist in the free state in nature, but is found native in combination with oxygen as boric acid, H_3BO_3, with sodium as borax, $Na_2B_4O_7.10H_2O$, with calcium as borocalcite, $CaB_4O_7.4H_2O$, and with both sodium and calcium as boronatrocalcite, $Na_2B_4O_7.2CaB_4O_7.18H_2O$. It is also found in smaller quantities in a number of other minerals, in sea water, and in the ash of a few plants.

Boron is known in two allotropic modifications. A compound of boron and aluminum, Al_2B_6, was formerly supposed to be the pure element, and bore the name of graphitoidal boron.

1. Amorphous Boron is prepared by heating in a crucible a mixture of 10 parts boron trioxide, B_2O_3, with 6 parts sodium, covered with 5 parts of sodium chloride:

$$B_2O_3 + 3Na_2 = 3Na_2O + B_2.$$

The fused mass, when cold, is treated with diluted hydrochloric acid, which leaves the boron undissolved, as a brown amorphous powder.

This variety is odorless and tasteless, and somewhat soluble in water, imparting to it a yellow color, from which solution it is precipitated unchanged on the addition of an acid. While this variety of boron is permanent in air or oxygen at ordinary temperatures, it readily oxidizes when heated, and may even burn, forming boron trioxide and small quantities of boron nitride, BN; the latter compound is the result of a union of boron with nitrogen of the air. When air is excluded boron may be heated to whiteness without melting; fusion may, however, be accomplished by a strong electric current.

Both nitric and hydrochloric acids oxidize boron to boric acid; and when the element is fused with sodium hydrate, borax is formed.

2. Adamantine Boron. This variety is prepared by fusing boron trioxide with aluminum :

$$B_2O_3 + Al_2 = Al_2O_3 + B_2.$$

The boron cryystallizes as the mass cools and is separated by dissolving the aluminum in sodium hydrate. This variety of boron is in the form of yellow or brownish-yellow crystals, having a specific gravity of 2.68. In this form boron is not pure but contains carbon and aluminum in a proportion corresponding to the formula $B_{48}Al_3C_2$.

The crystals are very hard, being next to the diamond in this respect, and withstand a red heat without change. They are unacted upon by hydrochloric, nitric, or nitrohydrochloric acids. When fused with sodium hydrate they are slowly changed to sodium borate, with evolution of hydrogen. Boron is one of the few elements which unite directly with nitrogen.

BORON AND HYDROGEN.

Boron Hydride, BH_3, is obtained by first fusing together boron trioxide and magnesium, whereby an impure magnesium boride is formed. The fused mass is then treated with diluted hydrochloric acid, when the following reaction takes place:

$$B_2Mg_3 + 6HCl = 3MgCl_2 + 2BH_3.$$

Considerable hydrogen is given off at the same time, but the boron hydride is recognized by its peculiar odor and nauseating effects when inhaled.

It is a colorless gas, which burns with a green flame, yielding boron trioxide and water. The gas is somewhat soluble in water, to which it imparts its peculiar odor.

BORON AND CHLORINE.

Boron Trichloride, BCl_3. When chlorine is passed over amorphous boron, combination takes place with evolution of heat and light. Crystallized boron requires to be heated before combination takes place. In practice dry chlorine is passed over boron trioxide and charcoal, heated to redness:

$$B_2O_3 + 3Cl_2 + 3C = 2BCl_3 + 3CO.$$

The escaping compounds mixed with some chlorine are passed through a freezing mixture, by which the boron trichloride is condensed. The latter is then finally freed from chlorine by agitation with and distillation from mercury.

Properties.—Boron trichloride is a colorless, mobile, strongly refracting liquid. Its specific gravity at 17° is 1.35. On the application of heat it boils at 18.23°. It fumes in the air, and is decomposed by water into hydrochloric and boric acids.

Similar compounds are known with bromine, BBr_3, and with fluorine, BF_3; the latter has a powerful affinity for water and chars organic matter like sulphuric acid.

BORON AND OXYGEN.

BORON TRIOXIDE.

Formula, B_2O_3. *Molecular Weight*, 69.68.

Preparation.—This oxide is formed when boron is burned in air or oxygen, but it is usually prepared by heating boric acid to redness:

$$2H_3BO_3 = B_2O_3 + 3H_2O.$$

The liquid should be poured out into thin layers and, when cold, broken into pieces of suitable size.

Properties.—Boron trioxide, when first prepared, is a colorless, transparent, vitreous solid, becoming opaque when exposed to air, owing to absorption of moisture. Its specific gravity at 4° is 1.83. At a white heat it is volatilized. On account of this ability to withstand high temperatures, it decomposes carbonates, nitrates, sulphates, and many other salts, converting them into borates. It is, therefore, much used in blowpipe work and in certain metallurgical operations.

BORIC ACID.

Formula, H_3BO_3. *Molecular Weight*, 61.78.

History.—This acid was first prepared and used in 1702 by Homberg, who obtained it by treating borax with a mineral acid. It was known under the name of sedative salt, or *sal sedativum Hombergii*. In 1774, Höfer, a Florentine apothecary, discovered the acid in the waters of the Tuscan lagoons, and some years later manufactories were established for its preparation, but were not successful until 1828, when the escaping jets of steam in the vicinity were utilized in the evaporation of the water.

Occurrence.—Boric acid occurs in the free state in nature. In the volcanic districts of Tuscany there are found numerous jets of steam issuing from crevices in the ground termed *suffoni* or *fumeroles*. This steam contains considerable quantities of boric acid. The number of these jets is often increased by boring. Boric acid is also found in considerable quantity combined with sodium, as borax, or tincal, on the borders of certain lakes in Thibet and Persia. Borax is also found in Clear Lake and Death Valley in California, and near Pyramid Lake in Nevada. The acid is further found in the mineral borocalcite, as calcium borate, in the nitre beds of Peru, and in some other districts combined with both sodium and calcium as boronatrocalcite.

Preparation.—A number of the fumeroles are surrounded by a wall of solid masonry and the enclosure filled with water, which condenses the steam and becomes charged with boric acid, at the same time the water is heated and evaporates. As the solution becomes stronger, it is allowed to run into similar tanks where the operation of saturation and evaporation is continued until the solution is strong enough to be run into leaden tanks in which the concentration is completed by steam from the fumeroles.

In the United States so much borax is found that it has been used for furnishing the acid by decomposition with hydrochloric acid:

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3.$$

This is effected by dissolving 1 part of borax in 2½ parts of boiling water and adding an excess of strong hydrochloric acid. On cooling, the boric acid crystallizes out and is purified by recrystallization.

Properties.—Boric acid (**Acidum Boricum,** U. S. P.) consists of "transparent, colorless scales, of a somewhat pearly lustre, or, when in perfect crystals, six-sided, triclinic plates, slightly unctuous to the touch, odorless, having a faintly bitterish taste, and permanent in the air." Its specific gravity at 15° is 1.4347. It is soluble in 25.6 parts of water, and in 15 parts of alcohol at 15°; in 3 parts of boiling water and in 5 parts of boiling alcohol. The alcoholic solution burns with a green flame.

Glycerin is also an excellent solvent for boric acid, 1 part of the acid dissolving in 10 parts of this solvent. The preparation known as boroglycerin is made by dissolving 62 parts of boric acid in 92 parts of glycerin at a temperature of 150°, and maintaining that heat until the mixture weighs 100 parts.

At 100° boric acid loses one molecule of water and is converted into metaboric acid, HBO_2. The latter is a white powder, and is slowly volatilized when maintained at the above temperature for a long time. When boric acid is kept at a temperature of 160° for some time, pyroboric acid ($H_2B_4O_7$) is produced, according to the following reaction:

$$4H_3BO_3 = H_2B_4O_7 + 5H_2O.$$

It is a brittle, vitreous mass, and is also known under the name of tetraboric acid.

Boric acid forms weak combinations with phosphoric, sulphuric, and some other acids, which indicate that it sometimes plays the part of a base. "The aqueous solution of boric acid colors blue litmus paper red, but yellow turmeric paper brownish-red after drying, even when the solution has been acidulated with hydrochloric acid; this brownish-red color is changed to bluish-black by ammonia water."

Impurities and Tests.—The most probable impurities are chloride and sulphate of sodium, and certain metals derived from the vessels used in the process of manufacture, like copper, lead, and iron. Chlorides may be detected by silver nitrate forming a white precipitate insoluble in nitric acid, sulphates by an equally insoluble precipitate with barium chloride, and the metals by a blackening with ammonium sulphide.

The most characteristic test for the acid is the green color it imparts to the flame of its alcoholic solution.

Borates.—Boric acid is tribasic, and its salts are very unstable; the best known one is magnesium borate, $Mg_3(BO_3)_2$. It, however, forms a number of salts with organic bases. The compounds of a few bases with metaboric acid are more stable, although not used or well known. The most familiar borates are those of pyroboric acid, which are very stable, and one of them, borax, $Na_2B_4O_7$, is extensively used.

Borax possesses the ability, when fused with different metallic oxides, of forming double salts of characteristic colors. It is on this property that the use of borax in blowpipe analysis depends, since by their action and color when brought into a borax bead on the end of a platinum wire many metals are detected.

Boron Trisulphide, B_2S_3, is formed when sulphur vapor is passed over heated amorphous boron; or a more practical method is to pass the vapor of carbon disulphide over a heated mixture of boron trioxide and charcoal:

$$2B_2O_3 + 3CS_2 + 3C = 2B_2S_3 + 6CO.$$

Boron trisulphide is a yellowish-white, friable, vitreous solid, easily decomposed by water into hydrogen sulphide and boric acid:

$$B_2S_3 + 6H_2O = 2H_3BO_3 + 3H_2S.$$

Boron Nitride, BN, is prepared by the direct union of amorphous boron and nitrogen at a white heat. This is interesting because of the indisposition of nitrogen to combine directly with any other element. Boron nitride is prepared more economically by heating to redness, in a platinum crucible, a mixture of one part anhydrous borax and two parts of dry ammonium chloride:

$$Na_2B_4O_7 + 4NH_4Cl = 2NaCl + 4BN + 2HCl + 7H_2O.$$

The fused mass is washed with water and hydrochloric acid, to remove the salt and some boric acid, which is mixed with the nitride.

Boron nitride is a white, light, amorphous powder, which phosphoresces in a gas flame with a greenish-white light. It is decomposed when heated in a current of steam into boric acid and ammonia:

$$BN + 3H_2O = H_3BO_3 + NH_3.$$

Boron nitride is infusible and unchanged, even at the melting point of nickel. It is not affected by nitric or hydrochloric acids, nor by alkaline solutions. Chlorine has no effect on it at a red heat. On fusion with potassium hydrate it evolves ammonia.

CHAPTER VII.

THE CARBON GROUP.

SILICON.

Symbol, Si. *Atomic Weight*, 28.3. ***Valence***, **IV.**

History.—The oxide of this element was early recognized as a distinct substance. Berzelius, in 1810, first isolated the element by fusing together iron, carbon, and silica. The crystallized variety was prepared by Deville in 1854, and its properties were investigated by himself and Wöhler.

Occurrence.—Next to oxygen, silicon is the most abundant element known. It is not found in the free state, but in combination with oxygen in quartz it is widely distributed. It is, further, the chief constituent of nearly all rocks, and consequently, also, of the soils which have resulted from the decomposition of rocks. It is also found in the ashes of many plants, having assisted to make up their mineral structure. Silicon exists in two allotropic conditions, the ***amorphous*** and the ***crystalline.***

Preparation.—Amorphous silicon is best prepared by heating to redness 10 parts of dry potassium silico-fluoride with 8 parts of potassium in an iron tube:

$$K_2SiF_6 + 4K = 6KF + Si.$$

The action is somewhat violent at first; when this is ended, the mass is allowed to cool, and then treated with hot water to remove potassium fluoride. The product is an amorphous, brown powder, which, when heated in the air, ignites and burns with the formation of the dioxide, SiO_2.

Silicon is insoluble in water and acids, except hydrofluoric, which dissolves it readily.

The crystalline variety is prepared by throwing, in small portions at a time, into a red-hot Hessian crucible a mixture of 15 parts of potassium silico-fluoride and 5 parts of sodium, then 36 parts of granulated zinc are quickly added, and the mass is covered with sodium chloride. The crucible is then maintained at a temperature just below the boiling point of zinc (1040°) for some time. The cooled mass is treated successively with hydrochloric, boiling nitric, and hydrofluoric acids, which leaves th crystals of silicon undissolved, as these are distinctly more refractory than the amorphous variety.

Properties.—When thus prepared, silicon is in the form of dark, lustrous, octohedral crystals, with a specific gravity of 2.49, and a degree of hardness sufficient to scratch glass. They withstand a white heat without igniting, and resist the action of all acids, except a mixture of hydrofluoric and nitric, which, when hot, dissolves them slowly. Hot concentrated solution of sodium hydrate dissolves silicon with formation of sodium silicate and evolution of hydrogen.

Silicon Hydride, SiH_4, is prepared by treating magnesium silicide with hydrochloric acid:

$$Mg_2Si + 4HCl = 2MgCl_2 + SiH_4.$$

The magnesium silicide is prepared by fusing together 40 parts of anhydrous magnesium chloride, 35 parts of dried sodium silicofluoride, 10 parts of fused sodium chloride, and 20 parts of sodium.

Silicon hydride is a colorless gas, which may be collected over water or mercury. When pure, the gas does not inflame spontaneously, but if mixed with hydrogen or warmed, it takes fire. In burning it evolves dense fumes of silicon dioxide, SiO_2, with formation of water at the same time. When mixed with chlorine, it explodes spontaneously.

Silicon Tetrachloride, $SiCl_4$, may be formed by burning silicon in chlorine, but is usually prepared by heating a mixture of silicon dioxide and carbon in a current of chlorine:

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO.$$

Silicon tetrachloride is a colorless, fuming liquid, having the specific gravity, at 0°, of 1.52, and boiling at 59.5°. It is decomposed by water into hydrochloric and silicic acids:

$$SiCl_4 + 4H_2O = H_4SiO_4 + 4HCl.$$

Silicon Hexachloride, Si_2Cl_6, is formed in small quantity when the vapor of silicon tetrachloride is passed over silicon heated to 1000°. It is a colorless, fuming liquid, which solidifies at —1°, and boils at 146°. Its specific gravity is 1.58 at 0°. It possesses the peculiarity of decomposing between 350° and 1000°, while above the latter and below the former temperature it is stable.

Silicon Chloroform, $SiHCl_3$, is produced when silicon is heated to redness in a stream of hydrochloric acid gas:

$$Si + 3HCl = SiHCl_3 + H_2.$$

It is a colorless, inflammable liquid, burning with a green-edged flame.

Silicon Bromoform, $SiHBr_3$, and Silicon Iodoform, $SiHI_3$, have also been prepared.

Silicon Tetrabromide, $SiBr_4$, is produced by passing bromine vapor over silicon dioxide and carbon, heated to low redness.

It is a colorless, heavy, oily liquid, which at 13° solidifies to a crystalline mass. It boils at 154°, and has a specific gravity of 2.81. It is decomposed into silicic and hydrobromic acids on the addition of water.

Silicon Hexabromide, Si_2Br_6, is a crystalline compound, prepared similarly to silicon hexachloride. It readily melts on the application of heat and boils at 240° without decomposition.

Silicon Tetraiodide, SiI_4, is prepared by passing vapor of iodine mixed with carbon dioxide over red-hot silicon. The carbon dioxide carries off the vapor of the tetraiodide as fast as formed and thus prevents its decomposition.

Silicon tetraiodide is a colorless, crystalline solid, soluble in carbon disulphide, and decomposed by water into silicic and hydriodic acids.

Silicon Hexaiodide, Si_2I_6, is formed by heating the tetraiodide with silicon to 280°. It is a crystalline solid, which fuses with decomposition at 250°, and is decomposed by water.

Silicon Tetrafluoride, SiF_4, is prepared by heating silicon dioxide with fluor spar and sulphuric acid:

$$SiO_2 + 2CaF_2 + 2H_2SO_4 = SiF_4 + 2CaSO_4 + 2H_2O.$$

Silicon tetrafluoride is a colorless, very pungent gas, which, under a pressure of thirty atmospheres or at a temperature of —107°, condenses to a liquid and at still lower temperatures solidifies. It is decomposed by water into silicic and hydrofluosilicic acids:

$$3SiF_4 + 4H_2O = H_4SiO_4 + 2H_2SiF_6.$$

Hydrofluosilicic acid, H_2SiF_6, is formed when the vapor of silicon tetrafluoride is led into water. The gelatinous silicic acid, which separates at the same time, would quickly stop the tube, if it were not prevented by keeping the latter under mercury, on the surface of which is placed the water. Each bubble of escaping gas forms a mass of silicic acid as it enters the water from the mercury. The hydrofluosilicic acid is obtained in aqueous solution, which fumes in contact with the air, and is decomposed by boiling into silicon tetrafluoride and hydrofluoric acid. It is useful as a laboratory reagent, since it forms a number of insoluble salts termed hydrofluosilicates, among which are those of potassium, lithium, and barium.

SILICON DIOXIDE.

SILICA.

Formula, SiO_2. *Molecular Weight*, 60.22.

This compound of silicon is the most abundant of all those in which the element occurs. There are three well-defined varieties of silica. Two of them are crystalline and one is amorphous. The most abundant of these is represented by *quartz*, which, when pure, consists of colorless, transparent, hexagonal crystals, having a specific gravity of 2.6, and represented in the scale of hardness by 7. It is sometimes slightly colored, as in amethyst, smoky quartz, and rose quartz.

Many of our most abundant rocks, as granite, gneiss, and syenite, are made up chiefly of quartz. It is also largely represented in sand and sandstone.

The second variety, also crystalline, is known as *tridimite*, which was originally found in Mexico, but is also distributed through a number of trachytic rocks. It occurs in hexagonal plates, having a specific gravity of 2.3, and a hardness the same as quartz.

The third variety is amorphous, the type of which is *chalcedony*. It has a specific gravity of 2.3. This variety frequently occurs with varying amounts of coloring impurities, as shown in *agate*, *jasper*, and *flint*. The precipitated silica formed when silicon fluoride is passed into water and dried, or when a soluble silicate is treated with an acid, the precipitate collected and dried, also belongs to this variety. In this form it possesses a specific gravity of 2.2; if, however, it be strongly heated for some time the specific gravity becomes 2.3. The quartz crystal likewise changes in specific gravity, when finely powdered and heated, from 2.6 to 2.3. An amorphous form known as *kiesel guhr*, or diatomaceous earth, occurs in large deposits near Berlin, Germany, and in several localities in the United States. *Opal* is a hydrated silicic oxide, as is also *geyserite*. Silicon dioxide is also found widely distributed in the vegetable and animal kingdoms, although not in such large amounts as among minerals. In the stalks of various grasses, and in the hair of man and animals, it is an important constituent.

The silicified wood found in many localities, but especially in the vicinity of the Yellowstone National Park in this country, is formed by silicon replacing the carbon of the wood.

All the varieties of silica are insoluble in water and acids, except in hydrofluoric acid, which dissolves them all. Quartz, even in fine powder, is practically insoluble in boiling solutions of the alkaline hydrates or carbonates, while the other two varieties will dissolve, the amorphous variety completely. This serves to distinguish quartz from the other two. All varieties on fusing with dry sodium or potassium carbonate form soluble silicate of the alkali:

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2.$$

On treating this solution of sodium silicate with acid, evaporating to dryness, adding water, collecting the precipitate, and washing thoroughly with boiling water, the purest amorphous silica is obtained.

All varieties of silica are extensively used by man. Quartz crystal and sand are largely used in the manufacture of pottery and glass; many of the colored varieties are used as gems; the amorphous kiesel guhr is employed as an absorbent of nitroglycerin, forming dynamite; and agate, on account of its hardness, goes to make mortars for the use of chemists.

Silicic Acid, H_4SiO_4. When hydrochloric acid is added to a dilute solution of sodium silicate, no precipitate occurs. If this solution be submitted to dialysis the sodium chloride and excess of hydrochloric acid will pass through, while a transparent colorless solution remains, supposed to contain orthosilicic acid, H_4SiO_4. This solution may be concentrated until it contains 14 per cent. of silica; a further concentration causes it to solidify into a jelly-like mass. This acid is represented in a few silicates, as *olivine*, Mg_2SiO_4, and *zircon*, $ZrSiO_4$. When the above clear solution of silicic acid is evaporated in a vacuum at 15°, a glass-like residue remains, supposed to consist of metasilicic acid, H_2SiO_3; on drying these two acids at a higher temperature silicon dioxide and water result:

$$\begin{aligned} H_4SiO_4 &= H_2O + H_2SiO_3. \\ H_2SiO_3 &= H_2O + SiO_2. \end{aligned}$$

A large number of metasilicates are known, a very abundant one being *enstatite*, Mg_2SiO_3. The best known one is perhaps sodium silicate, Na_2SiO_3. A number of silicates occur in which the base is combined with a multiple of the formula possessed by the above acid, with various proportions of water. Such compounds are known as *polysilicates*, and make up the large number of naturally occurring silicates.

Silicates.—Apart from those silicates occurring native and those manufactured for special purposes, like glass, we have one official, namely, sodium silicate, or soluble glass, **Liquor Sodii Silicatis.** This is prepared by fusing together sodium carbonate and sand, and allowing the resulting liquid mass to run into water, which causes it to solidify in smaller and more porous pieces, so that it may afterward be more easily dissolved in water. It is found in commerce in almost all degrees of concentration, from a thin, transparent liquid to a thick gelatinous mass. [illegible]

U. S. P. directs that which has a specific gravity of 1.3 to 1.4. This strength contains from 10 to 12 per cent. of sodium and 20 to 24 per cent. of silica. It is used largely in bandaging.

Glass.—When sand, lime, and potassium carbonate are fused together in proper proportions a transparent, insoluble substance results, known as glass. Bohemian glass is a silicate of potassium and calcium. It is very difficult to fuse, and resists the action of most chemicals. Crown or window glass is a silicate of calcium and sodium with small quantities of aluminum and iron. Bottle or green glass is similar in composition with less sodium and more calcium. It also contains more iron. Flint glass is a silicate of potassium and lead. It is quite fusible, and is chiefly valuable on account of its high refractive power, which makes it applicable in the manufacture of lenses.

Detection.—Soluble silicates are detected by the gelatinous precipitate that is produced on the addition of an acid ; and both soluble and insoluble silicates are recognized by means of the salt of phosphorus bead, which, when held in the blowpipe flame with silica or a silicate, becomes opaque and is found to contain a floating mass, known as the *silica skeleton*, which is very characteristic.

Silicon Disulphide, SiS_2. When a mixture of silica and carbon is heated to whiteness, and vapor of carbon disulphide led over it, there are formed long, silky crystals of the above compound, which decompose on the addition of water into hydrogen sulphide and silicic acid.

Silicon Carbide, SiC. This compound is known as carborundum, and has come into use as a polishing agent because of its excessive hardness, which is said to equal that of the diamond.

CARBON.

Symbol, C. *Atomic Weight*, 11.97. *Valence*, IV.

History.—Carbon in the form of charcoal has been known from the earliest times. Graphite was thought to be identical with molybdenite, and the diamond was supposed to be a kind of quartz crystal. In 1779 Scheele pointed out the difference between molybdenite and graphite, and concluded that the latter must be looked upon as a kind of mineral coal. Numerous experiments were carried out in the latter half of the last century to determine the composition of the diamond.

A number of investigators subjected it to high temperatures and observed that it disappeared, and, at the suggestion of Lavoisier, a diamond in a glass vessel over mercury was ignited by means of a burning-glass, and the fact noted that carbon dioxide was produced. Davy, some years later, combined the carbon dioxide produced by the combustion of a diamond with calcium, and by reducing the calcium carbonate obtained pure carbon.

Occurrence.—Carbon exists in the free state in nature in three allotropic modifications,—crystallized, as *diamond* and *graphite*, and amorphous, as coal. Diamonds are found in Brazil, Georgia, California, New South Wales, and South Africa.

Graphite is distributed throughout the world. A very good quality is found in the North of England. Large deposits occur in Germany, in Southern Siberia, in Ceylon, at Ticonderoga, in New York, at Sturbridge, in Massachusetts, and at Sonora, in California.

Coal is found in nearly all parts of the world.

In combination, carbon is found in petroleum and in natural gas, in nearly all vegetable and animal matter, and, combined with calcium as carbonate, in marble, limestone, and chalk.

(1) Diamond.—Diamonds occur either in alluvial deposits supposed to have resulted from the decomposition of certain kinds of metamorphic rock, or else loose in sand. When found they are usually covered with an opaque layer. This surface is removed and the gem given a great number of faces by cutting and polishing. These faces are so formed as to reflect the greatest amount of light. This is accomplished by so arranging the back planes or faces that nearly all the light strikes them at an angle greater than 24° 13', when it is all reflected. Diamond dust is used in the cutting and polishing.

The diamond belongs to the regular or isometric system of crystallization, the prevailing form being the octohedron. It has a specific gravity of 3.5 to 3.6, and is the hardest substance known, being rated as 10 on the scale of hardness. It is insoluble in all known liquids.

The weight of the diamond is usually stated in carats, a carat being equal to 3.17 grains, or 0.204 gramme. A variety of black diamond from Brazil, which is worthless as a gem, is much used in drilling rocks. The specific gravity of the black variety is less than that of the transparent one, being about 3.0.

On the application of heat diamonds remain unchanged in an atmosphere of hydrogen or when air is excluded, even at a white heat; but the intense temperature of the electric current causes them to swell to a mass of coke or graphite. At these temperatures in air or oxygen combustion takes place, carbon dioxide being formed, and a small quantity of ash remaining. This ash, which consists of silica and ferric oxide, amounts to from 0.05 to 0.20 per cent.

The diamond is a poor conductor of electricity and heat.

The clearest specimens of the diamond become of great value when properly cut and polished. One of the finest is the "Pitt" or "Regent" diamond, which weighs 136 carats and is valued at $600,000. A number of larger ones have been found, but the weight after cutting rarely exceeds 250 carats.

(2) Graphite. This substance, which is also known as plumbago or black lead, occurs in crystalline form, not well defined, but frequently approaching hexagonal prisms. It may also be made artificially by adding to melted cast-iron a considerable quantity of charcoal, which on cooling is deposited as crystals of graphite.

Graphite possesses a black metallic lustre. It feels soft and greasy between the fingers, and leaves a black mark when drawn across paper. Its specific gravity varies from 1.84 to 2.50. On the application of heat it remains unchanged, when air and oxygen are excluded, but at very high temperatures, in a stream of oxygen, it is slowly consumed, with more difficulty, however, than the diamond.

The amount of ash which remains on ignition is variable, being from 1 to 10 per cent. In the purer varieties there are also present from .5 to 1.3 per cent. of hydrogen.

Graphite is purified by digesting 1 part, on a water-bath at 60°, with 3 parts of potassium chlorate, and sufficient nitric acid to render the mixture fluid, or the graphite is allowed to stand for twenty-four hours with a mixture of potassium chlorate and sulphuric acid. The product is washed with water and heated, when it swells up with a violent evolution of gas, and there finally results a very fine powder of pure graphite. Hydrofluoric acid is sometimes used in the purification, in order to dissolve and render volatile the silica.

Graphite when mixed with fire clay is used for making the black-lead or plumbago crucibles. It is also useful as a polishing agent and in the manufacture of lead-pencils. For this latter purpose the purified powder is mixed with a fine clay, and by the aid of water made into a plastic mass. The mixture is then forced through small holes by powerful pressure, which gives the leads the desired shape. The long cylinders are then cut into the required lengths and enclosed in wood

(3) Amorphous Carbon. Under this head may be included the following varieties: (*a*) Gas carbon, (*b*) Coke, (*c*) Wood charcoal, (*d*) Animal charcoal, (*e*) Lampblack.

(*a*) Gas carbon is found in the upper part of the retorts in which coal is heated in the preparation of illuminating gas. It occurs in iron-gray masses of a metallic lustre, and possesses considerable hardness. It varies in specific gravity from 1.75 to 2.50, according to the distance from the surface of the retort. It is a good conductor of electricity, and is used for the carbon plates in several forms of batteries. Sometimes it is used for the carbon pencils in the arc electric light.

(*b*) Coke is a by-product in the manufacture of illuminating gas. It remains in the retort after the volatile portions, which go to make gas, have been driven off by destructive distillation. Large quantities of coal in the United States are converted into coke in special coking ovens and the volatile products allowed to escape. The answer to the inquiry about the wastefulness of the process is that the coke is more valuable than the coal, and there is not the demand for the volatile products to make it remunerative to retain them.

Coke occurs in irregular, brittle, porous masses, of a grayish, somewhat metallic lustre. It does not burn so easily as coal, and requires a constant draught of air. Its combustion is attended with great heat and but little smoke. It is extensively used in metallurgical operations. The composition of coke is about 91 per cent. pure carbon, 5 to 6 per cent. of ash, with varying proportions of oxygen, hydrogen, and nitrogen.

(*c*) Wood charcoal usually goes under the simple name of charcoal. Pure charcoal is obtained when sugar is burned in a platinum or porcelain dish, and it is purified in a current of chlorine. It is tasteless, insoluble, conducts electricity, and has a specific gravity of 1.57.

Wood charcoal is prepared by the incomplete combustion of wood. This is accomplished by covering piles of wood with earth and igniting at suitable openings. By regulating the access of air slow combustion takes place, water, some carbon dioxide, and various other products escape, and charcoal remains. In the preparation of wood alcohol and acetic acid the process of charring wood is carried out in large iron retorts, so that the volatile products are saved. It has been found, however, that temperature below that necessary to produce charcoal is best for preparing the volatile products.

The yield of charcoal is from 17 to 20 per cent. when made in the ordinary way, but by the use of super-heated steam to regulate the temperature, and maintaining it at 300°, the yield may be increased to 33 per cent. The proportion of carbon in the product, however, is diminished, being only about 65 per cent., while the oxygen, hydrogen, and nitrogen are correspondingly increased. By increasing the temperature to 400° the yield is decreased to 20 per cent., and the carbon in the product increased to 80 per cent. At 1000° the yield is 18.7 per cent., and the carbon in the product 82 per cent. A larger yield is obtained when the process is carried out slowly and when the wood is dry.

The most esteemed charcoal for pharmaceutical purposes is prepared from willow twigs two or three years old. It is official as **Carbo Ligni,** U. S. P.

The best charcoal is hard and brittle, breaking with a lustrous fracture and emitting a metallic sound when struck. As ordinarily prepared it is a poor conductor of heat and electricity, but when prepared at a high temperature it is more compact and becomes a better conductor. Like all other varieties of carbon, it is infusible. Wood charcoal possesses in a marked degree the power to absorb and condense gases. One volume of boxwood charcoal was found by Hunter to absorb the following volumes of gases under ordinary pressure and at a temperature of 0°:

	Volumes.		Volumes.
Hydrogen	4.4	Nitric oxide	70.5
Nitrogen	15.2	Ethene	74.4
Oxygen	17.9	Nitrous oxide	86.3
Carbon monoxide	21.2	Cyanogen	107.5
Carbon dioxide	67.7	Ammonia	171.7

On account of this property charcoal becomes valuable for absorbing noxious gases and destroying them. It also possesses the power of decolorizing dark liquids, although not in the same degree as the next variety.

(*d*) Animal charcoal is prepared by charring bones and other animal matter. The variety known as bone-black is formed when bones are heated in closed iron retorts; the by-product in this case is "Dippel's animal oil." Animal charcoal is official in two forms, **Carbo Animalis,** U. S. P., and **Carbo Animalis Purificatus,** U. S. P. The crude article is in dull-black, granular fragments or powder; it is odorless and tasteless and insoluble in water or alcohol. When ignited it should leave about 86 per cent. of a white ash, consisting of calcium phosphate and carbonate, which should be completely soluble in hydrochloric acid with the aid of heat. The purified animal charcoal is prepared by digesting in a water-bath for twenty-four hours two parts of the crude preparation with three parts of hydrochloric acid and fifteen parts of water, washing, drying, and heating to dull redness.

When purified, animal charcoal is a dull-black powder, odorless, tasteless, insoluble in water and all other solvents. When ignited at a high temperature, with a little mercuric oxide and free access of air, it should leave only a trace of residue. Purified animal charcoal possesses the power of absorbing coloring matter from solution. It will withdraw the color from solutions of indigo or logwood, and remove the fusel oil from alcohol. It absorbs alkaloids and astringent compounds from their solutions, and gives them up to boiling alcohol. Many of the domestic filters for the purification of water are constructed of animal charcoal and sand. Perhaps the most extensive application of animal charcoal is in the decolorizing of sugar, and in the purification of the heavy portions of petroleum, by which such preparations as petrolatum are made.

(*e*) Lampblack. This variety of carbon is in very fine powder. It is obtained from the smoky flame of many bodies rich in carbon, as resins, when their combustion takes place without much access of air, and the products are condensed. This condensation is accomplished by passing the products through a series of chambers. Rosin and petroleum are most frequently employed in the preparation of lampblack, but the product is not pure. The purification is effected by heating for some time in a current of chlorine. A very pure lampblack is made from the natural gas of Western Pennsylvania and Ohio. The product from this last source is very pure and is sometimes known under the name of *diamond black*. Lampblack, when pure, is a velvety black, impalpable powder, having a specific gravity of 1.729 at 17°. It should mix readily with water, and yield no color to alcohol and ether when agitated with them, showing the absence of oily impurities. It is used to give a black color to paints and inks, not only on account of its intense black color, but also because of its indestructibility.

COAL.

Coal is classified as a variety of carbon, although it contains, besides that element, considerable quantities of oxygen, hydrogen, nitrogen, mineral matter, and frequently sulphur.

Our present supply is the product from the decomposition of plants of a former age, this decomposition having taken place under great pressures without access of air, and in the presence of moisture.

Owing to the differences under which their formation took place, we have several different varieties of coal. They may, however, be arranged into two classes, *Anthracite* and *Bituminous* coals.

Anthracite is found in this country most abundantly in Pennsylvania, and in lesser amount in Rhode Island. An inferior variety is found in Wales, France, Saxony, and Southern Russia. It contains about 90 per cent. of carbon and only very small quantities of sulphur. It is hard, with a conchoidal fracture and an iron-black color, frequently displaying iridescence. It burns with but little flame and gives out an intense heat. The volatile matter is contained in it in small amount, being from 6 to 7 per cent.

Bituminous coal is found in all parts of the world. It is much softer than anthracite, and contains a larger proportion of volatile matter. It is used extensively in producing coke and in the manufacture of illuminating gas, in which process it yields many useful by-products.

Cannel coal is a variety of this class which, on account of its large proportion of volatile matter, is much used in England for gas making. The carbon of bituminous coal varies from 70 to 91 per cent., the sulphur from 0.40 to 2.25 per cent., the nitrogen from 1.00 to 2.50 per cent., and the ash from 0.75 to 20 per cent.

Lignite is a brown coal of more recent formation than the two preceding varieties. It frequently retains the structure of the wood from which it was formed.

Jet is a variety of this brown coal, so compact as to take a fine polish.

CARBON AND HYDROGEN.

These two elements unite directly with each other, although with some difficulty and always under peculiar conditions. The number of such compounds, mostly formed by indirect means, however, is very great. These compounds of carbon and hydrogen, when associated with oxygen and nitrogen, become well-nigh innumerable, and make up the material of *Organic Chemistry*.

The subject of organic chemistry, therefore, is confined to the consideration of the compounds of carbon and their derivatives, and the classification of these is based on several series of *hydrocarbons*, or compounds of carbon and hydrogen.

It will be sufficient at this point to give some description of two or three compounds of these two elements in order to have them for comparison with the hydrogen compounds of the preceding elements.

METHANE.

MARSH GAS.

Formula, CH_4. *Molecular Weight*, 15.97.

Marsh gas is the first member of the *paraffin series* of hydrocarbons. It occurs free in nature wherever vegetable matter is undergoing decomposition in the presence of moisture. This is always noticeable where leaves and other vegetable matter are under water, and the bubbles which rise when such a mass is disturbed are composed chiefly of this gas. It also occurs in coal seams, giving rise to the *fire damp* of the miners, and is the explosive element in mine disasters. The very lightest part of petroleum consists largely of this gas, and escapes as soon as the oil is relieved of its pressure on coming to the surface. Closely associated with this is the *natural gas*, which has marsh gas for its chief constituent. Natural gas is found in great abundance in Pennsylvania, Ohio, West Virginia, and Indiana. In all these places it has been successfully used for heating, and, after treatment, also for lighting. It has been found especially valuable in metallurgical operations. The supply, which at first seemed inexhaustible, has in the past few years perceptibly diminished, and it is only a question of some years more, in many localities, when a return will be made to other fuels.

Preparation.—Marsh gas may be prepared by heating sodium acetate and hydrate in an iron or copper retort, when the following reaction takes place :

$$\underset{\substack{\text{Sodium}\\\text{Acetate.}}}{NaC_2H_3O_2} + \underset{\substack{\text{Sodium}\\\text{Hydrate.}}}{NaOH} = \underset{\substack{\text{Sodium}\\\text{Carbonate.}}}{Na_2CO_3} + \underset{\substack{\text{Marsh}\\\text{Gas.}}}{CH_4}.$$

In practice it is preferable to substitute calcium oxide for a part of the sodium hydrate, thereby preventing the mixture from liquefying. This is best accomplished by using sodium acetate, 1 part, and soda-lime, 4 parts. Soda-lime is made by slaking calcium oxide with a solution of sodium hydrate of such strength that 2 parts of calcium oxide shall be mixed with 1 part of sodium hydrate. The mixture is then dried and heated in an iron or Hessian crucible, after which it is preserved in a tightly-closed bottle.

Marsh gas may be obtained absolutely pure by adding zinc methyl to water:

$$\underset{\text{Zinc Methyl.}}{Zn(CH_3)_2} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Zinc Hydrate.}}{Zn(OH)_2} + \underset{\text{Marsh Gas.}}{2CH_4.}$$

Another method of preparation consists in passing a mixture of carbon disulphide vapor and hydrogen sulphide over red-hot metallic copper:

$$\underset{\text{Hydrogen Sulphide.}}{2H_2S} + \underset{\text{Carbon Disulphide.}}{CS_2} + \underset{\text{Copper.}}{8Cu} = \underset{\text{Copper Sulphide.}}{4Cu_2S} + \underset{\text{Marsh Gas.}}{CH_4.}$$

This process is of interest because of the fact that every one of the compounds employed is strictly inorganic and may be made directly from elementary matter, thus rendering it possible to prepare many of what are considered organic compounds synthetically.

Properties.—Marsh gas is colorless, odorless, and tasteless, and is insoluble in water. At a pressure of 54.9 atmospheres and a temperature of —81.8° the gas liquefies. This liquid commences to boil at —164° under ordinary atmospheric pressure. Marsh gas is combustible, and when mixed with 2 volumes of oxygen or 10 volumes of air it explodes with considerable violence. By the electric spark the gas is slowly decomposed into its constituent elements. When a mixture of 1 volume of marsh gas and 2 volumes of chlorine is exposed to direct sunlight or the flame of a taper, a sudden reaction takes place, with the formation of hydrochloric acid, and the separation of carbon as a black, very finely divided powder. Marsh gas is not considered poisonous, since when mixed with air to the extent of 9 per cent. it has been inhaled by workmen in coal mines without serious inconvenience.

ETHENE.

OLEFIANT GAS.

Formula, C_2H_4. *Molecular Weight*, 27.94.

This gas is the first member of the second series of hydrocarbons, known as the *olefine series*, to which it has given the name.

Preparation.—The gas is best prepared by heating, in a capacious glass flask, a mixture of 1 part of alcohol with 6 parts of sulphuric acid; when the gas is evolving rapidly a further quantity of a mixture of 1 part alcohol and 2 parts acid is run slowly in, so as not to cool the contents of the flask sufficiently to retard the evolution of the gas. In this way a large yield is obtained from the smallest amount of materials. The gas should be washed by passing it through concentrated sulphuric acid to remove vapors of alcohol and ether, and then through solution of potassium hydrate to remove carbon dioxide. The reaction involved may be expressed as follows:

$$\underset{\text{Alcohol.}}{C_2H_6O} = \underset{\text{Ethene.}}{C_2H_4} + \underset{\text{Water.}}{H_2O.}$$

The sulphuric acid simply plays the part of a dehydrating agent, and brings about the reaction by its affinity for the water.

Properties.—Ethene, or ethylene, is a colorless gas, having a peculiar, suffocating, ethereal odor. Its specific gravity is 0.9709. At a temperature of 10.10° and a pressure of 51 atmospheres it liquefies, and boils at —103° under ordinary atmospheric pressure. It is soluble in 8 parts of water. Ethylene is an easily combustible gas, burning with a very luminous flame and evolving much smoke. It forms a mixture with 3 volumes of oxygen, which explodes violently on the application of flame. It forms an oily liquid with an equal volume of chlorine, which is known as the "oil of the Dutch chemists." From this the name of "olefiant gas" is derived.

ACETYLENE.

ETHINE.

Formula, C_2H_2. *Molecular Weight*, 25.94.

Preparation.—Acetylene may be prepared by the direct union of carbon and hydrogen. This is accomplished when the carbon electrodes of a powerful battery approach each other in an atmosphere of hydrogen. It also results whenever there is imperfect combustion of substances rich in carbon and hydrogen.

Properties.—Acetylene is a colorless gas, with a peculiar, disagreeable odor. It is condensed to a liquid at 1° and under a pressure of 48 atmospheres. It is moderately soluble in water. Acetylene is combustible, burning with a bright but smoky flame.

ILLUMINATING GAS.

COAL GAS.

History.—Gas was first used for illuminating purposes in the house of William Murdock, at Redruth, in Cornwall, England. He distilled coal in an iron retort, and lighted his house with the gas which he thus manufactured. This occurred about 1792. Gas was used for lighting the streets of London in 1812, and those of Paris in 1815.

Preparation.—Illuminating gas is prepared by the destructive distillation of bituminous coal, although occasionally some other substances rich in carbon, like rosin, are used.

The process is accomplished in iron or fire-clay retorts, ten to twelve feet in length and two or three feet in diameter. Usually five of these retorts are placed in a furnace together. The temperature employed approaches low redness.

The products of this dry distillation are: (1) coke, (2) water, (3) tar, (4) ammonium carbonate, (5) liquid hydrocarbons, (6) hydrogen sulphide, (7) carbon dioxide, (8) carbon monoxide, (9) sulphur dioxide, (10) hydrogen, (11) marsh gas, (12) olefiant gas, and some other gaseous hydrocarbons.

Of these, 8, 10, 11, and 12 are useful for combustion and illumination; 1 is valuable for fuel; 3, 4, and 5 have other uses, to be considered later. The volatile products are first passed into the hydraulic main, where the water and tar are separated. From thence the gas goes into condensers, in which more tarry and oily liquids are removed. It then passes into the scrubbers, which consist of one or more columns of coke over which a spray of water trickles; this serves to wash the gas and remove ammonia. Next come the purifiers, in which the gas comes in contact with dry calcium hydrate or ferric hydrate, which serves to remove the sulphur compounds and carbon dioxide. From the purifiers the gas goes into the gasometers for storage and distribution.

The average yield per ton of coal is from ten to twelve thousand cubic feet.

Coal gas is considerably lighter than air, its specific gravity varying from 0.65 to 0.75.

The value of gas for illuminating purposes is determined by comparing the light from a jet burning five feet per hour with the light from a sperm candle consuming one hundred and twenty grains per hour. Such a gas flame should be equal to thirteen or fourteen candles.

CARBON AND OXYGEN.

There are two well-known compounds of these two elements:

Carbon monoxide, CO.
Carbon dioxide, CO_2.

CARBON MONOXIDE.

Formula, CO. *Molecular Weight*, 27.93.

This compound is formed when coal burns with an incomplete supply of air. It may be easily recognized in the combustion of anthracite coal by its peculiar blue flame. Almost identical with this formation of it is the one by passing carbon dioxide over red-hot charcoal :

$$CO_2 + C = 2CO.$$

The carbon may be replaced by iron and the same result attained. Carbon monoxide is most easily prepared by heating oxalic acid and concentrated sulphuric acid together :

$$H_2C_2O_4 = CO_2 + CO + H_2O.$$

The sulphuric acid acts by its affinity for water, and so causes a breaking down of the oxalic acid molecule.

The mixed gases are passed through a strong solution of sodium hydrate to absorb the carbon dioxide.

In a similar manner formic acid, or a formate, may be decomposed by sulphuric acid ; in this case, however, no carbon dioxide is formed :

$$HCHO_2 = CO + H_2O.$$

An economical method and one that will yield the gas rapidly consists in heating finely powdered potassium ferrocyanide with eight or ten times its weight of strong sulphuric acid :

$$\underset{\text{Potassium Ferrocyanide.}}{K_4Fe(CN)_6} + \underset{\text{Sulphuric Acid.}}{6H_2SO_4} + \underset{\text{Water.}}{6H_2O} = \underset{\text{Potassium Sulphate.}}{2K_2SO_4} + \underset{\text{Ammonium Sulphate.}}{3(NH_4)_2SO_4} + \underset{\text{Ferrous Sulphate.}}{FeSO_4} + \underset{\text{Carbon Monoxide.}}{6CO.}$$

As soon as the reaction commences the heat must be removed and the vessel cooled, if necessary, in order to prevent too rapid evolution of the gas. The water necessary in the above reaction is derived from the water of crystallization in the potassium ferrocyanide and from the small quantity in the commercial sulphuric acid.

Properties.—Carbon monoxide is a colorless gas, with a peculiar odor. It is very slightly soluble in water and has no effect on litmus paper. It readily burns in air or oxygen with a peculiar pale-blue flame, the product of its combustion being carbon dioxide :

$$CO + O = CO_2.$$

When added to half its volume of oxygen, a mixture is formed which explodes on the application of flame.

The action of carbon monoxide on the human system is that of a narcotic poison. A small amount in the air is sufficient to produce giddiness and headache, followed by insensibility. Its peculiar action appears to be due to the formation of a compound with the hæmoglobin of the blood, the latter acquiring a purplish color.

CARBON DIOXIDE.

Formula, CO_2. *Molecular Weight*, 43.89.

History.—Carbon dioxide was discovered by Paracelsus about 1520, and was further investigated by Van Helmuth in the early part of the seventeenth century. Its chemical nature was first made out by Lavoisier.

Occurrence.—Carbon dioxide occurs free in the atmosphere to the extent of three or four volumes in ten thousand. It is found in many mineral waters, and in the craters of some extinct volcanoes. Combined with various bases as carbonates it is still more abundantly distributed. The principal one of these compounds is calcium carbonate, which, as marble, limestone, and chalk, is one of the most abundant of minerals.

Preparation.—Carbonates and bicarbonates when heated yield the gas according to the following:

$$CaCO_3 = CaO + CO_2.$$
$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

When small quantities are desired it is rapidly and conveniently made from marble and hydrochloric acid:

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

The same result may be attained by the use of sulphuric acid, but the calcium sulphate which is formed is quite insoluble, and therefore difficult to remove from the flask.

When a current of air is passed over red-hot carbon the product is carbon dioxide, provided the air be kept in excess. This and the method by heating a carbonate are used for furnishing the gas in the manufacture of carbonates on the large scale.

Properties.—Carbon dioxide is a colorless gas with a faint odor and weak acid taste. It is 1½ times heavier than air and 22 times heavier than hydrogen. 1 volume of water dissolves 1 volume of the gas at ordinary atmospheric pressure. This solubility of the gas is increased 1 volume for every increase of 1 atmosphere in pressure.

A solution containing about 5 volumes of the gas in water constitutes the so-called "soda-water" which is dispensed in the pharmacies of this country. This solution is prepared by generating the gas from marble dust and sulphuric acid, in closed copper generators, and, after purifying the gas by passing it through water containing sodium bicarbonate, it is passed into water in steel cylinders, which are constantly agitated in order to facilitate the absorption. Only porcelain-lined steel cylinders and block-tin pipes should be used. Lead and copper are dissolved by the solution. It was formerly the custom to store the solution in copper cylinders lined with tin. In such vessels the soda-water frequently becomes contaminated with copper. The water should give no coloration with ammonium hydrate or sulphide, and no precipitate with potassium ferrocyanide, thus indicating the absence of copper.

The gas is more soluble in alcohol than in water.

Under a pressure of 38.5 atmospheres at a temperature of 0° carbon dioxide is condensed to a colorless, mobile liquid. This liquid has a specific gravity of 0.923 at 0°, and 0.782 at 20°. It is not miscible with water, and has no action on dry litmus paper. When liquid carbon dioxide is suddenly released from pressure, such an intense degree of cold is produced as to cause a portion of the liquid to solidify. This solidification may also be accomplished by cooling the liquid to —65°. This solid carbon dioxide is capable of producing an intense degree of cold; to accomplish this the solid is mixed with ether and placed under the receiver of an air pump. On account of the rapid vaporization of the oxide a temperature of —110° is produced. This solid may be handled with safety, as it is always surrounded by a thin layer of the gas; when, however, it is pressed into contact with the skin it will cause a blister.

Carbon dioxide is neither combustible nor a supporter of combustion. This property may be illustrated by lowering a lighted taper into a vessel of it, or, since it is heavier than air, by pouring it down an inclined board on which are placed a number of lighted candles. Under the name of "choke damp" it sometimes collects in old wells, and is detected by lowering a lighted candle, which will be extinguished if the gas is present. This choke damp results from the explosion of marsh gas in mines and frequently fatally supplements the destruction caused by the latter.

When present in the atmosphere to the extent of 1 per cent inconvenience in breathing is experienced, and 10 per cent. will cause insensibility. Its deleterious action on respiration results from the exclusion of oxygen rather than from any inherent poisonous property of the gas. It may be taken into the stomach in aqueous solution with advantage in many cases.

Carbon dioxide when dissolved in water appears to form a definite compound, carbonic acid, as follows :

$$\underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Carbonic}\\\text{Acid.}}}{H_2CO_3}.$$

This solution reddens litmus paper, and is decomposed by heat, the gas escaping with effervescence.

Uses.—Carbon dioxide is employed in the manufacture of carbonates ; its solution in water is extensively used as a beverage ; and it forms an important constituent of the chemical fire extinguishers. Apart from these, and on a much larger scale, it assists in the growth of plant life. Large quantities of it are thrown into the atmosphere by man and animals ; it is there decomposed by the chlorophyll of plants aided by sunlight ; the carbon resulting from this decomposition goes to make up the structure of the plant, while the oxygen is rejected and returns to maintain the proper proportion of that element in the atmosphere.

Carbonates.—The salts of carbonic acid are usually prepared by passing carbon dioxide into a solution of a hydrate of the base :

$$2KOH + CO_2 = K_2CO_3 + H_2O,$$

or they are formed by double decomposition between a soluble carbonate and a soluble salt of the base :

$$\underset{\substack{\text{Sodium}\\\text{Carbonate.}}}{5Na_2CO_3} + \underset{\substack{\text{Magnesium}\\\text{Sulphate.}}}{5MgSO_4} + \underset{\text{Water.}}{6H_2O} = \underset{\text{Magnesium Carbonate.}}{(MgCO_3)_4,Mg(OH)_2.5H_2O} +$$
$$\underset{\substack{\text{Sodium}\\\text{Sulphate.}}}{5Na_2SO_4} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{CO_2}.$$

The carbonates of the alkalies are soluble in water, all others are insoluble. The acid carbonates of the alkalies and the alkaline earths are soluble in water and all others are insoluble.

The carbonates of the alkalies, alkaline earths, and some metals are quite stable ; the acid carbonates are decomposed on heating and by boiling their aqueous solutions.

Detection.—Carbonates are detected by the escape of carbon dioxide on the addition of a weak acid. The escaping gas causes a precipitate when passed into a solution of calcium hydrate, which precipitate redissolves on the further addition of the gas.

PRACTICAL EXERCISES.

(1) Place a few pieces of marble (calcium carbonate) in a flask arranged as for the preparation of hydrogen, cover with water, and add hydrochloric acid; a brisk evolution of carbon dioxide occurs. The gas may be collected over water, although it is somewhat soluble in that liquid; it may also be collected by downward displacement, as it is considerably heavier than air.

(2) Pour some clear lime water into a jar of the gas and agitate; the solution immediately becomes cloudy, owing to the formation of insoluble calcium carbonate. If the gas be passed in for some time the liquid will become nearly clear again, on account of the solubility of the precipitate in excess of carbonic acid.

(3) Add solution of potassium hydrate to a test-tube or jar of the gas, close, and agitate well; the gas is absorbed by the alkali, as may be shown by placing the vessel under water and removing the stopper, when the water will rush in, nearly filling it.

(4) A lighted taper lowered into the gas is immediately extinguished. The same result is accomplished by pouring the gas into the vessel some distance above the flame and allowing the gas to settle down upon it. The latter experiment also illustrates the weight of the gas, which is twenty-two times heavier than hydrogen.

COMBUSTION AND ILLUMINATION.

1. Chemical Nature of Combustion.—This is in all ordinary cases a combination of the burning body with oxygen, supplied by the air, which is the usual supporter of combustion. This is readily established by examining the products of combustion, which in these cases are oxides. They may be solids as with the products of the combustion of metals, liquids as in the case of hydrogen oxide, or water, or gases as in the case of the oxides of carbon.

As these combustions involve direct chemical union of the elements concerned, it matters not which is the combustible body and which the supporter of combustion. We may in many cases easily reverse the ordinary conditions. Thus, a jet of hydrogen or illuminating gas will burn in an atmosphere of air or oxygen because the hydrogen or the hydrocarbons of the illuminating gas combine chemically with the oxygen. For the same reason, a jet of oxygen will burn in an atmosphere of hydrogen or illuminating gas if such be arranged. A jet of air will also burn in the atmosphere of illuminating gas, the air being for the time called the combustible body and the illuminating gas the supporter of combustion.

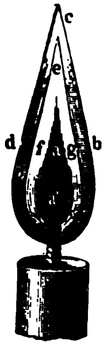
2. Conditions of Combustion.—Combustion may be slow or rapid, accompanied by flame or not, according to conditions.

The appearance of flame indicates a burning gas, which may be given off even when solids or liquids are taken, in consequence of the heat. A certain temperature is necessary for flame. The temperature of a gaseous combustion may be so lowered that the flame is extinguished. For instance, metallic gauze has this effect upon a flame because of its excellent conducting powers whereby the temperature is rapidly lowered. If a piece of gauze is pressed down upon a lighted gas-jet the flame will not penetrate the gauze, or if the gas be lighted above the gauze the flame will not communicate to the gas issuing below. The Davy safety-lamp is an application of this principle.

3. **The Structure of Flame.**—An ordinary candle flame or gas-jet, as shown in Fig. 57, is composed of several cones. The inner cone contains gaseous hydrocarbons not as yet ignited, the middle cone contains an excess of carbon rendered incandescent at the temperature of the flame, while the outer cone is bluish and has no unconsumed carbon.

The fact that unconsumed hydrocarbon gases exist in the inner cone of a gas flame can be demonstrated by introducing a small glass tube obliquely from one side and taking off this gas to be burned. A phosphorus match may also be held with the head placed in this point of no combustion, and the phosphorus composition will melt but not ignite until withdrawn and allowed to come in contact with the air.

FIG. 57.

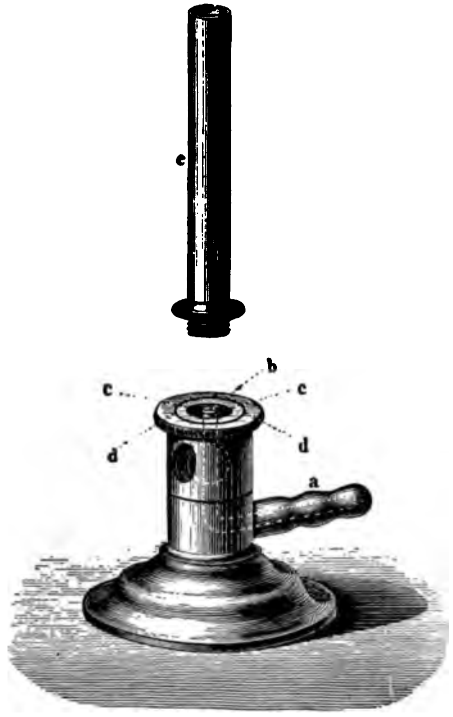


Candle flame.

4. **Distinction between Luminous and Non-Luminous Flames.**—While, as stated, the appearance of flame indicates a burning gas, the luminosity of the flame depends upon the separation in the flame of small solid particles rendered incandescent by the heat. Thus, in the ordinary gas flame we have particles of carbon separated and rendered incandescent. If sufficient oxygen or air be admitted to the cone of the flame, the hydrocarbon gases will be consumed without separation of carbon. This may be done in either one of two ways,—by the aid of the blowpipe or blast lamp, which directs a current of air directly into the cone of the flame, or by mixing air with the illuminating gas before it is burned, as in the Bunsen burner.

The mouth blowpipe is often used for the purpose of directing a small but very hot flame upon any object. We are capable of getting two quite distinct chemical effects by its aid. If the long pointed blowpipe flame be examined it will be seen that we have an inner and an outer blue cone. If the substance to be heated be placed just within the bounds of the inner cone, we get a reducing effect; that is, it is deoxidized, because of the deficiency of oxygen here; if, on the other hand, the substance be heated by the outer cone of the flame, we get an oxidizing effect, because of the excess of oxygen present in this part of the flame.

FIG. 58.



Bunsen burner.

The Bunsen burner, as shown in Fig. 58, is a most convenient form of apparatus for changing a luminous flame into a non-luminous one. As seen in the illustration, the gas first issues from a small jet. Here it would tend to burn with the yellow luminous flame. But a tall chimney is screwed on to an outer casing surrounding the jet and air is admitted through openings in the base of this chimney. The gas issuing from the inner jet produces a strong upward draft in the chimney, and a mixture of gas and air therefore rises and is ignited at the top of the chimney.

Two methods of changing the non-luminous flame into a luminous flame exist. We may pass a gas like hydrogen over volatile hydrocarbons, like benzene, petroleum-ether, or naphthalene, and so enrich it with hydrocarbon vapors, or we may direct a hot non-luminous flame like that of the oxyhydrogen blowpipe upon solids like caustic lime, which are thereby rendered incandescent. Both methods are of practical application, as in the carburetting of water-gas and in the production of the "lime-light."

CARBON AND SULPHUR.

CARBON DISULPHIDE.

Formula, CS_2. *Molecular Weight*, 75.93.

Carbon disulphide was discovered by Lampadius in 1796. It is prepared by a direct union of the elements at a red heat. For this purpose a cast-iron cylinder or earthenware retort is filled with charcoal, and heated to redness; sulphur is then introduced at the bottom; the vapor rising combines with the carbon and passes over into a series of condensers. Some hydrogen sulphide is formed at the same time, which is removed by agitation with mercury. The carbon disulphide is then redistilled. Fat or wax is sometimes added to the liquid before redistillation in order to assist in the removal of the more offensive-smelling compounds of sulphur.

Properties. — Carbon disulphide is a colorless, mobile, strongly-refracting liquid, which, as it comes in commerce, usually has a fetid odor, due to various sulphur impurities, but when purified as above described, is of a mild ethereal odor. It is insoluble in one thousand parts of water, but mixes in all proportions with absolute alcohol, ether, chloroform, and the fixed and volatile oils. It solidifies at —116° and melts at —110°. Its vapor is very inflammable, taking fire in the air at 149°; this may be effected by bringing a test tube of paraffin heated to this temperature in contact with it. The result of its combustion is carbon dioxide and sulphur dioxide:

$$CS_2 + 3O_2 = CO_2 + 2SO_2.$$

The vapor when mixed with nitrogen dioxide readily burns, on the application of flame, with a peculiar bluish flame, which is very rich in actinic rays. The vapor acts as a poison on man and animals, even in very small amount; if it be inhaled for some time it will produce serious effects upon the nervous system.

Uses.—Carbon disulphide is used extensively in the arts on account of its great solvent action on oils and rubber. It has been extensively used in France to destroy the grape pest or *Phylloxera*. For the latter purpose it is often first converted into a sulphocarbonate of sodium. (See also *Xanthogenates* under Organic Chemistry.)

Detection.—Carbon disulphide is detected by mixing a small quantity of the liquid with alcoholic ammonia, and evaporating on a water-bath, when ammonium sulphocyanate is formed :

$$\underset{\substack{\text{Carbon}\\\text{Disulphide.}}}{CS_2} + \underset{\text{Ammonia.}}{4NH_3} = \underset{\substack{\text{Ammonium}\\\text{Sulphocyanate.}}}{NH_4SCN} + \underset{\substack{\text{Ammonium}\\\text{Sulphide.}}}{(NH_4)_2S}.$$

On acidifying the residue with hydrochloric acid, and adding ferric chloride solution, the red color of ferric sulphocyanate is developed.

Sulphocarbonic or Thiocarbonic Acid, H_2CS_3.—When sodium hydrate is brought in contact with carbon disulphide, the sodium salt of thiocarbonic acid is formed :

$$\underset{\substack{\text{Sodium}\\\text{Hydrate.}}}{6NaOH} + \underset{\substack{\text{Carbon}\\\text{Disulphide.}}}{3CS_2} = \underset{\substack{\text{Sodium}\\\text{Thiocarbonate.}}}{2Na_2CS_3} + \underset{\substack{\text{Sodium}\\\text{Carbonate.}}}{Na_2CO_3} + \underset{\text{Water.}}{3H_2O}.$$

The free acid is obtained when hydrochloric acid is added to ammonium thiocarbonate :

$$(NH_4)_2CS_3 + 2HCl = 2NH_4Cl + H_2CS_3.$$

This acid is a yellowish-brown, heavy oil, which easily decomposes, when heated, into hydrogen sulphide and carbon disulphide :

$$H_2CS_3 = H_2S + CS_2.$$

The thiocarbonates of the alkalies and alkaline earths are soluble in water. The potassium salt mixed with carbonate is obtained when carbon disulphide is added to potassium hydrate solution, and is used as a remedy against *phylloxera*. Its action depends on the carbon disulphide which is liberated when the mixture comes in contact with earth.

Carbonyl Sulphide, COS, is supposed to exist in some sulphur waters. It may be obtained by the direct union of carbon monoxide and sulphur vapor, when passed through a red-hot tube ; but it is more easily made by acting on potassium sulphocyanate with sulphuric acid :

$$\underset{\substack{\text{Potassium}\\\text{Sulphocyanate.}}}{KCNS} + \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{2H_2SO_4} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Acid Ammo-}\\\text{nium Sulphate.}}}{NH_4HSO_4} + \underset{\substack{\text{Acid Potas-}\\\text{sium Sulphate.}}}{KHSO_4} + \underset{\substack{\text{Carbonyl}\\\text{Sulphide.}}}{COS}.$$

It is a colorless gas, with a disagreeable, sulphuretted odor ; very inflammable, burning with a bright blue flame. It is soluble in an equal volume of water, and this solution gradually decomposes into carbon dioxide and hydrogen sulphide :

$$COS + H_2O = CO_2 + H_2S.$$

CHAPTER VIII.

CLASSIFICATION OF THE ELEMENTS.

PERIODIC SYSTEM.

REFERENCE has been made in a previous section to a comprehensive classification of the elements. While this has hitherto been based on valence in the main, it can now be made to cover much more and to indicate many additional points of relationship between the elements.

Elements showing similarity of properties have for many years been classed together in groups or families, and the gradations of properties within these groups were noticed to correspond with the regular increase in atomic weights of the elements. But it was not until 1869 that these peculiar relations were embodied in what is called the *periodic law.*

Mendelejeff and Lothar Meyer in 1869–1870 independently observed that if the elements were arranged according to their increasing atomic weights, elements showing similarity of properties will recur after certain intervals. Thus *the properties of the elements are periodic functions of the atomic weights.*

A glance at the table on the following page will show that the elements following hydrogen in atomic weight are arranged in two periods of seven, Li to F and Na to Cl, and the succeeding elements in periods of seventeen, the elements at the beginning and at the end of both large and small periods showing almost complete analogy in physical and chemical properties, while all the members of the large periods present as complete an analogy in their corresponding elements. Thus K, Rb, and Cs show perfect agreement with Li and Na, Zn and Cd with Be and Mg; likewise there is the same analogy at the ends of the periods, Br and I being clearly members of the same group as F and Cl, while in the middle of the large periods Zn and Cd and Ga and In are in perfect accordance. In this table, if we read horizontally we have the several smaller and larger periods indicated. When we read vertically we have, by reason of the recurrence of similar elements, the valence groups indicated. It is possible, also, in these vertical columns to indicate sub-groups, as, for instance, in the second column we have the alkaline earths as one sub-group and the beryllium and magnesium group as another

PERIODS.	SERIES.	GROUP I. — R_2O	GROUP II. — RO	GROUP III. — R_2O_3	GROUP IV. RH_4 RO_2	GROUP V. RH_3 R_2O_5	GROUP VI. RH_2 RO_3	GROUP VII. RH R_2O_7	GROUP VIII. — RO_4		
									RO_4	RO_4	RO
(1)	1	H 1	—	—	—	—	—	—			
	2	Li 7	Be 9	B 10.9	C 12	N 14	O 16	F 19			
(2)	3	Na 23	Mg 24.3	Al 27	Si 28.3	P 31	S 32	Cl 35.4			
(3)	4	K 39	Ca 39.9	Sc 44	Ti 48	V 51.2	Cr 52	Mn 54.8	Fe 55.9	Co 58.6	Ni 58.6
	5	Cu 63	Zn 65	Ga 70	Ge 73	As 75	Se 79	Br 79.7			
(4)	6	Rb 85.2	Sr 87.3	Y 88.9	Zr 90.4	Cb 93.7	Mo 95.9	— 100	Ru 101.4	Rh 102.9	Pd 106.4
	7	Ag 107.7	Cd 111.5	In 113.6	Sn 118.8	Sb 119.6	Te 125	I 126.5			
(5)	8	Cs 132.7	Ba 136.9	La 138.2	Ce 139.9	Di 142	—	—	—	—	—
	9	—	—	—	(Er 166)?	—	—	—			
(6)	10	—	—	Yb 172.6	—	Ta 182	W 183.6	—	Os 190.3	Ir 192.5	Pt 194.3
	11	Au 196.7	Hg 199.8	Tl 203.7	Pb 206.4	Bi 208.9					
	12				Th 231.9		U 238.8				

sub-group. Both the hydrogen valence and the oxygen valence are separately recognized in the headings of the vertical columns. The many breaks in the list indicate hypothetical elements that may yet be discovered.

Both physical and chemical properties may be determined to a very marked degree by the periodic law. This is very clearly shown in the cases of the measurable physical properties, which manifest either a maximum or a minimum in the middle of both large and small periods, as may be seen in considering the specific gravities of some of the elements:

	Na	Mg	Al	Si	P	S	Cl
Specific gravity,	.67	1.7	2.5	2.5	2.	1.9	1.3

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	As	Se	Br
.86	1.6	3.8	—	5.5	6.8	7.2	7.9	8.5	8.8	8.8	7.1	5.9	5.6	4.6	2.9

Also in the case of the chemical properties, maxima and minima may be shown in the case of valence, the hydrogen valence being at the maximum in the middle of the period, thus:

I.	II.	III.	IV.	III.	II.	I.
NaR	MgR_2	AlR_3	SiH_4	PH_3	SH_2	ClH

While in the case of the salt-forming oxides the maximum valence increases with the small periods, thus:

II.	II.	III.	IV.	V.	VI.	VII.
Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7

And in the large periods increases with a double periodicity:

I.	II.	III.	IV.	V.	VI.	VII.
K_2O	CaO	Sc_2O_3	TiO_2	V_2O_5	CrO_3	Mn_2O_7

VI.	IV.	II.
FeO_3	CoO_2	NiO

I.	II.	III.	IV.	V.	VI.	VII.
Cu_2O	ZnO	Ga_2O_3	—	As_2O_5	SeO_3	Br_2O_7

On account of the gradations in properties of the elements the existence, position, and properties of undiscovered elements may be predicted. In general the value of any property of an element is the mean between the values of the same property of the elements on all four sides of it in the table. When this table was first prepared there were gaps between boron and yttrium, between aluminum and indium, and between silicon and tin. To these hypothetical elements Mendelejeff assigned the names of eka-boron, eka-aluminum, and eka-silicon, and minutely described their properties. In 1875, 1879, and 1886 gallium, scandium, and germanium were discovered respectively with the properties assigned by Mendelejeff.

The only explanation of the agreement in the properties of the elements with the atomic weights is that all the elements are aggregations of the same primordial substance. Hydrogen was once believed to be this substance, chiefly because of the fact that it looked at first as if the atomic weights of all the elements were simple multiples of the hydrogen atom. This has been shown to be incorrect by recent accurate atomic weight determinations. (See reference to Prout's law, p. 109.)

PART III.

CHEMISTRY OF THE METALS.

PART III.

CHEMISTRY OF THE METALS.

CHAPTER I.

THE ALKALI METALS.

General Characters.—The alkali group of metals consists of **Potassium, Sodium, Lithium, Rubidium, Cæsium,** and the atomic group **Ammonium.**

In this group, the valence of the individual members is the immediate reason for so classifying them. They have numerous other properties in common, for instance, their soft, wax-like consistence, their low specific gravity, all but rubidium and cæsium being lighter than water, their strong metallic lustre, and their low melting points. Of course, where the metals are to be compared, ammonium is excluded; but the compounds of all the members bear a close resemblance to one another. The metals all energetically decompose water, evolving hydrogen, and forming hydrates in solution which have a strongly alkaline reaction.

The salts are nearly all soluble in water, the chief exceptions being lithium phosphate and carbonate. Potassium, ammonium, rubidium, and cæsium form insoluble tartrates and chloroplatinates, while sodium and lithium do not. Some other distinguishing characters of their salts will be noted when they come to be treated analytically.

POTASSIUM.

Symbol, K. *Atomic Weight*, 39.1. *Valence*, I.

History.—The salts of potassium have been known from the earliest times. They were probably first extracted from wood ashes under the name *alkali*. Previous to 1736 there was no distinction between the salts of potassium and sodium. The former then became known as *potashes*.

The metal potassium was discovered in 1807 by Davy, who separated it by the electrolysis of potassium hydrate. Its elementary character was not finally admitted until 1811, after the investigations of Gay-Lussac and Thénard.

Occurrence.—Potassium is widely distributed in nature, but never in the metallic state. In the mineral kingdom it is found as nitrate or nitre, as the double magnesium and potassium chloride, or carnallite, and as the chloride, or sylvite. It occurs, however, most extensively as silicate in many rocks; especially in potash-feldspar, where it is found to the extent of 10 to 15 per cent. As feldspar is a constituent of granite, it will be seen that the distribution is very wide.

The other abundant rocks that contain potassium are syenite, gneiss, and micaceous schist. Many mineral waters, and the waters of the ocean, contain small proportions of the potassium salts.

Potassium is found abundantly in the vegetable and animal kingdoms. It is a necessary constituent of plants, and is absorbed by them from the soil. The condition in which it exists in the soil is usually as a compound with some organic acid. Plants obtain their supply of this element from the soil where it is stored. The soil retains more potassium than it does sodium. The animal body contains a considerable proportion of potassium salts. The salts of sodium are eliminated from the system while those of potassium are retained.

Sheep's wool contains nearly one-third its weight of potassium salts, which are known in commerce as *suint*.

Sources.—The world's supply of potassium salts is derived chiefly from the chloride and carbonate. The chloride of potassium is obtained from the carnallite and sylvite of Stassfurt, Germany. The output of chloride in 1891 was over 65,000 tons. A considerable quantity of the sulphate of potassium occurs at Stassfurt, with the chloride.

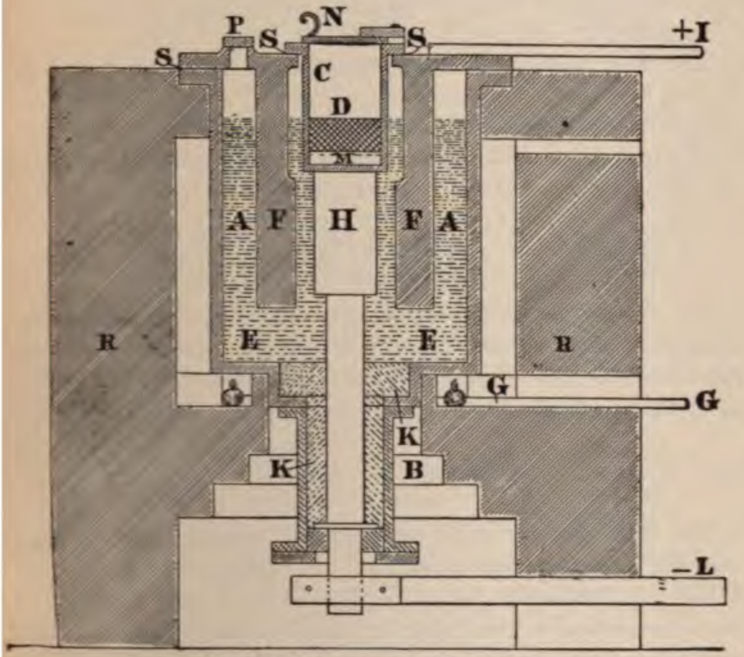
The carbonate is obtained from wood ashes, and the supply at the present time is chiefly furnished by Russia, although a distinct amount is produced in the United States and Canada. Small quantities of the carbonate are also obtained from the beet-root residues after the preparation of the sugar. The washings from sheep's wool, after evaporation and calcination, form an addition source for potassium salts in the form of carbonate.

Preparation.—Potassium may be prepared by subjecting so potassium hydrate to a strong electric current. The metal a ydrogen are liberated at the negative pole and oxygen at the ositive pole, as follows :

$$2KOH = K_2 + H_2 + O_2.$$

This process has been perfected by Castner, so as to render it vailable for producing the metal on a large scale. The apparatus y which this is accomplished is illustrated in Fig. 59.

FIG. 59.



Electrolytic preparation of potassium.

The iron vessel A contains the melted potassium hydrate, which is maintained in a fused condition by the gas-jets G. The negative electrode H is brought from the bottom, the positive electrode F is suspended from the top, and the two are separated by an iron wire cage. H is sealed in position by the metallic hydrate K below the gas-jets after it has cooled. The vessel and its attachments are supported by the brickwork R ; P is an aperture for the insertion of a thermometer, since it is important that the temperature of the hydrate be not allowed to rise more than twenty degrees above its fusing point.

When the decomposition takes place, the liberated potassium rises and floats on the surface of the fused hydrate in c. It is removed by a finely-perforated spoon, which retains the metal and allows the melted hydrate to run through. The process is a continuous one, as more of the hydrate is added from time to time to replace that which is decomposed.

Potassium may also be prepared by heating to whiteness a mixture of potassium hydrate and metallic iron:

$$\underset{\substack{\text{Potassium}\\\text{Hydrate.}}}{4KOH} + \underset{\text{Iron.}}{3Fe} = \underset{\substack{\text{Ferroso-ferric}\\\text{Oxide.}}}{Fe_3O_4} + \underset{\text{Potassium.}}{2K_2} + \underset{\text{Hydrogen.}}{2H_2.}$$

The older method for the preparation of the metal on a large scale is that in which an intimate mixture of potassium carbonate and carbon is heated to whiteness. This mixture is best prepared by the ignition of acid potassium tartrate in closed crucibles, when the following decomposition occurs:

$$\underset{\substack{\text{Potassium}\\\text{Bitartrate.}}}{2KHC_4H_4O_6} = \underset{\substack{\text{Potassium}\\\text{Carbonate.}}}{K_2CO_3} + \underset{\text{Water.}}{5H_2O} + \underset{\substack{\text{Carbon}\\\text{Monoxide.}}}{4CO} + \underset{\text{Carbon.}}{3C.}$$

The residue of potassium carbonate and carbon is mixed with a little more charcoal, and brought to a strong white heat in a furnace similar to that shown in Fig. 61, and used in the preparation of sodium. The reaction which takes place is as follows:

$$\underset{\substack{\text{Potassium}\\\text{Carbonate.}}}{K_2CO_3} + \underset{\text{Carbon.}}{C_2} = \underset{\text{Potassium.}}{K_2} + \underset{\substack{\text{Carbon}\\\text{Monoxide.}}}{3CO.}$$

The retort consists of a wrought-iron mercury flask covered with fire-clay to prevent oxidation. It is adapted to a flat receiver in order to facilitate rapid cooling and prevent the formation of a black compound of potassium and carbon monoxide. The liquid potassium as it condenses is allowed to run into petroleum, in order to preserve it from oxidation. This process was brought into practical operation by Brunner, but has since been improved upon by others, and very extensively employed. It is likely, however, to be superseded by the electrolytic method. The potassium prepared in this manner is still in need of purification by redistillation, as it is liable to be contaminated with carbon monoxide, which, unless removed, may give rise to the black explosive compound.

A method was devised by Castner, previously to his electrolytic one, in which it was proposed to furnish the metal at an expense not exceeding twenty-five cents a pound. This consists in first obtaining an iron carbide, FeC_2, an intimate mixture of fine iron and coke. This is then heated with potassium hydrate to about 800°, when the following reaction takes place:

$$\underset{\text{Potassium Hydrate.}}{6KOH} + \underset{\text{Iron Carbide.}}{FeC_2} = \underset{\text{Potassium Carbonate.}}{2K_2CO_3} + \underset{\text{Hydrogen.}}{3H_2} + \underset{\text{Iron.}}{Fe} + \underset{\text{Potassium.}}{K_2}$$

The potassium carbonate is reconverted into hydrate and used again.

Properties.—On account of the rapidity with which potassium combines with oxygen, it is found in commerce chiefly in the form of small globular pieces of the size of cherries, and preserved under petroleum or other hydrocarbon, to protect it from the air.

Potassium is of a waxy consistence, and when freshly cut exhibits the true appearance of the metal, which is silver white in color and of a bright metallic lustre. Next to lithium, it is the lightest metal known, having a specific gravity of 0.865. On the application of heat it melts at 62.5°, and at a low red heat, in an atmosphere of some inert gas like hydrogen or nitrogen, it volatilizes, yielding a greenish vapor.

By melting some of the metal in a tube surrounded by nitrogen gas, allowing to cool until a portion solidifies, and pouring out the liquid portion, that remaining in the tube takes the form of tetragonal octohedra, of a silver-white color.

Potassium dissolves in liquid ammonia, forming a deep blue solution, and, as the liquid evaporates, it is left unchanged.

Potassium has a strong affinity for oxygen, and its vapor bursts into flame on coming in contact with air, burning with a characteristic violet color. If air be absolutely free from moisture, it will not combine with the metal at ordinary temperatures. When thrown on water, the latter is immediately decomposed, the metal combining with the oxygen and liberating the hydrogen, which with some potassium vapor bursts into a violet-colored flame.

Potassium combines with the halogens with great energy; a small fragment dropped on bromine causes a violent explosion. It has the power to displace most other metals from their combinations, and has, therefore, been used for preparing magnesium and aluminum.

POTASSIUM AND HYDROGEN.

Potassium Hydride, K_4H_2.—When potassium is heated in an atmosphere of hydrogen to 300° a silver-white, brittle mass results, which begins to decompose at 410°, or, under reduced pressure, dissociation begins at 200°. Potassium hydride inflames spontaneously on contact with air.

POTASSIUM AND THE HALOGENS.

The halogen compounds of potassium are:

Potassium fluoride, KF.
Potassium chloride, KCl.
Potassium bromide, KBr.
Potassium iodide, KI.

Potassium Fluoride, KF, is prepared by neutralizing aqueous hydrofluoric acid, in a platinum dish, with potassium carbonate or hydrate. On concentrating the solution the salt crystallizes out in cubes. When formed at ordinary temperatures these crystals have the formula $KF.2H_2O$, but at or above 35° they form without water of crystallization.

The salt is deliquescent, and its solution attacks glass. Hydrofluoric acid has the property of forming acid salts; of these, the one with potassium, KHF_2, is characteristic. The other halogens appear not to have this property of forming acid salts.

Potassium Chloride, KCl.—This salt was first used in medicine by Sylvius de le Boë, under the name of *sal febrifugum* or *sal digestivum*. It occurs in sea water, in many mineral springs, and at Stassfurt, Germany. As carnallite, $KCl\,MgCl_2.6H_2O$, and sylvite, KCl, it is the most abundant salt in that locality.

Preparation.—Since potassium chloride occurs so abundantly in nature, it is rarely prepared on the small scale. It can, however, readily be made by neutralizing hydrochloric acid with potassium carbonate, according to the following reaction:

$$\underset{\text{Potassium Carbonate.}}{K_2CO_3} + \underset{\text{Hydrochloric Acid.}}{2HCl} = \underset{\text{Potassium Chloride.}}{2KCl} + \underset{\text{Carbon Dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O}.$$

On the large scale carnallite is mixed with three-fourths its weight of water, and the mixture treated for some time with live steam, whereby the carnallite is resolved into its constituent salts, magnesium chloride and potassium chloride. The hot solution is allowed to cool, and the less soluble potassium chloride crystallizes. It is further purified by washing with a little cold water and recrystallizing.

Properties.—Potassium chloride occurs in permanent, white, cubical crystals; soluble in 3 parts of cold water, in about 2 parts of hot water, and insoluble in alcohol. Its specific gravity at 15° is 1.945. On the application of strong heat the salt melts, and at a red heat it volatilizes.

Uses.—Potassium chloride is used for the preparation of a number of other potassium salts, notably the chlorate and carbonate. The impure salt is used largely as a fertilizer.

Potassium Bromide, KBr. **Potassii Bromidum, U. S. P.**—This salt is prepared by one of two methods:

(1) 1 part of iron wire in a large flask is covered with 10 parts of water; 2 parts of bromine are slowly added, in small portions at a time, allowing the combination with the iron to take place after each addition. This part of the operation should be conducted in a well-ventilated room, in order that the operator may avoid inhaling the irritating fumes that are unavoidably evolved. In the reaction which takes place ferrous bromide is formed, as follows:

$$Fe + Br_2 = FeBr_2.$$

The resulting solution is of a green color, and is then filtered from the excess of iron. It is then heated in an open dish to near the boiling point, and 1.75 parts of potassium carbonate in 10 parts of water are slowly added until, after heating a short time, the liquid reacts slightly alkaline. The result is a mixture of potassium bromide and ferrous carbonate:

$$\underset{\text{Ferrous Bromide.}}{FeBr_2} + \underset{\text{Potassium Carbonate.}}{K_2CO_3} = \underset{\text{Potassium Bromide.}}{2KBr} + \underset{\text{Ferrous Carbonate.}}{FeCO_3}.$$

The mixture is heated for some time in order to convert the bulky precipitate of ferrous carbonate into a more compact ferrous and ferric hydrate, carbon dioxide escaping at the same time. The whole is then filtered and the precipitate washed free of potassium bromide by means of hot water. The clear filtrate, containing the potassium bromide, is evaporated and crystallized.

(2) To a convenient quantity of potassium hydrate solution bromine is added in small portions at a time, until, after agitation, the yellow-brown color of the bromine remains permanent, indicating a slight excess of that element. The following reaction expresses what has taken place:

$$\underset{\text{Potassium Hydrate.}}{6KOH} + \underset{\text{Bromine.}}{3Br_2} = \underset{\text{Potassium Bromide.}}{5KBr} + \underset{\text{Potassium Bromate.}}{KBrO_3} + \underset{\text{Water.}}{3H_2O}.$$

The solution is evaporated nearly to dryness, and a quantity of wood charcoal stirred in amounting to one-tenth of the amount of bromine. The mixture is then dried and heated to low redness in an iron vessel, when the reduction of the potassium bromate is accomplished as follows:

$$KBrO_3 + 3C = KBr + 3CO.$$

The cooled mass is treated with water, the solution filtered and evaporated to crystallization.

Properties.—When perfectly pure, potassium bromide occurs in colorless, translucent, cubical crystals, permanent in the air, odorless, with a sharp saline taste and a neutral reaction. The commercial salt usually occurs in white, opaque crystals with a slightly alkaline reaction. The salt is soluble in 1.6 parts of water at 15°, and in less than one part of boiling water. It is soluble in 200 parts of cold and in 16 parts of boiling alcohol; also soluble in 4 parts of glycerin. When heated the salt decrepitates somewhat, and at 700° it fuses without decomposition. At a bright red heat it volatilizes, imparting to the flame a violet color.

Potassium bromide is identified by the usual potassium tests and by adding to 10 c.c. in a test-tube a few drops of chloroform and then, a little at a time, chlorine water until the solution smells distinctly of it; a yellowish-brown color is imparted to the chloroform on agitation. If a violet color be produced iodide is indicated. An admixture of potassium bromate is indicated when an immediate yellow color is assumed on the addition of diluted sulphuric acid. This test depends on the following reaction:

$$5KBr + KBrO_3 + 6H_2SO_4 = 6KHSO_4 + 3H_2O + 3Br_2.$$

Potassium Iodide, KI. **Potassii Iodidum, U. S. P.**—This salt is prepared by mixing in a capacious porcelain dish 1 part of iron wire with 8 parts of water, and adding in small portions at a time 3 parts of iodine. The result is ferrous iodide, as follows:

$$Fe + I_2 = FeI_2.$$

The greenish solution is filtered from the undissolved iron, and treated with 1 part of iodine, forming ferric iodide:

$$2FeI_2 + I_2 = Fe_2I_6.$$

To this solution are added 2.2 parts of pure potassium carbonate, previously dissolved in 10 parts of water. The following reaction takes place:

$$\underset{\text{Ferric Iodide.}}{Fe_2I_6} + \underset{\text{Potassium Carbonate.}}{3K_2CO_3} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Potassium Iodide.}}{6KI} + \underset{\text{Carbon Dioxide.}}{3CO_2} + \underset{\text{Ferric Hydrate.}}{Fe_2(OH)_6}.$$

If necessary a small additional quantity of potassium carbonate may be added until the solution is faintly alkaline. The whole mixture is then boiled for a few minutes, which causes the precipitate to become more dense; it is then filtered and washed. The filtrate and washings are concentrated to a small bulk and set aside for the potassium iodide to crystallize out.

Another method consists in adding to a convenient quantity of potassium solution sufficient powdered iodine in small portions at a time to produce a permanent yellowish color. Potassium iodide and iodate are formed as follows:

$6KOH$	+	$3I_2$	=	$5KI$	+	KIO_3	+	$3H_2O.$
Potassium Hydrate.		Iodine.		Potassium Iodide.		Potassium Iodate.		Water.

The solution is evaporated to a syrupy consistence, and a quantity of wood charcoal, equal to one-tenth the amount of iodine employed, is stirred in. The mixture is then dried and heated to low redness. The iodide is unchanged by this treatment, while the iodate is converted into iodide according to the following reaction:

$$KIO_3 + 3C = KI + 3CO.$$

The residue, after cooling, is treated with water, filtered, and the filtrate, after concentration, is set aside to crystallize.

Finally, potassium iodide is prepared from the "mother liquors" obtained in the preparation of sodium nitrate from Chili saltpetre, iodine being recovered as cuprous iodide, Cu_2I_2. This is converted into hydrogen iodide as follows:

$$Cu_2I_2 + H_2S = Cu_2S + 2HI.$$

The hydrogen iodide, after removal of cuprous sulphide by filtration, is neutralized with potassium carbonate.

Properties.—Potassium iodide is ordinarily found in large, white, opaque crystals, having been crystallized from a faintly alkaline solution. When the crystals are formed in neutral solutions, they are colorless and nearly transparent. The salt has a faint odor, and a sharp, saline taste with a faint, bitterish aftertaste. The crystals are permanent in dry air, but slightly deliquescent in moist air.

The salt is soluble in 0.75 part water at 15°, and in 0.5 part of boiling water, in 18 parts alcohol, and in 6 parts boiling alcohol; it is also soluble in 2.5 parts of glycerin.

When heated the salt decrepitates, and at a low red heat it fuses; at a bright red heat it volatilizes without decomposition. The aqueous solution should have a scarcely perceptible alkaline reaction towards litmus paper. The salt becomes of a faint yellowish color when exposed to the air, on account of the liberation of traces of iodine.

The usual tests for potassium serve to identify the salt as containing that base, and the iodine is indicated by adding a few drops of chloroform to the aqueous solution, and then chlorine water in small portions at a time until the solution smells of it, when, on agitation, a violet color will be imparted to the chloroform; iodine is also liberated from this salt by fuming nitric acid, by concentrated sulphuric acid, and by chromic acid. Silver nitrate produces a yellow precipitate of silver iodide when added to a solution of potassium iodide. This precipitate is insoluble in nitric acid and in ammonium hydrate.

Uses.—Potassium iodide is used largely in medicine.

Potassium Tri-iodide, KI_3.—When a concentrated solution of potassium iodide is saturated with iodine, a dark-brown liquid is formed, which when evaporated at ordinary temperatures over sulphuric acid, yields nearly black, acicular crystals, possessing a metallic lustre. These crystals are very deliquescent, melt at 45°, and at 100° decompose into potassium iodide and iodine. The solution of these crystals is a useful reagent for alkaloids. It usually gives brown precipitates, soluble in alcohol.

POTASSIUM AND OXYGEN.

There are two well-defined potassium oxides:

Potassium monoxide, K_2O.
Potassium peroxide, KO_2.

At least one other oxide, having the formula K_4O, is supposed to exist, but it has never been prepared pure, and when formed readily changes to the monoxide.

Potassium Oxide, K_2O, is obtained, together with some peroxide, by heating the metal in dry air. When this mixture is strongly heated it evolves oxygen and the monoxide remains. It is also prepared by heating the metal with potassium hydrate:

$$2KOH + K_2 = 2K_2O + H_2.$$

The oxide, when pure, is a white powder or brittle mass; it fuses at a high temperature and volatilizes somewhat. Its affinity for water is so intense that when moistened with that liquid it becomes red-hot. Potassium hydrate is the result of this combination with water.

Potassium Peroxide, KO_2, is obtained when the metal is heated with an excess of oxygen. It is a yellow mass which gives up oxygen when heated to whiteness. On treatment with water, it dissolves, with the formation of potassium hydrate, hydrogen peroxide, and oxygen.

The blue compound which is formed when potassium is burned with an insufficient amount of air is the suboxide, K_4O.

Potassium Hydrate, KOH. **Potassa, U. S. P.**—This compound, which is also known as potassium hydroxide and caustic potash, appears to have been first observed by Geber in the eighth century, and was considered to be an element until Davy demonstrated its compound nature in 1807.

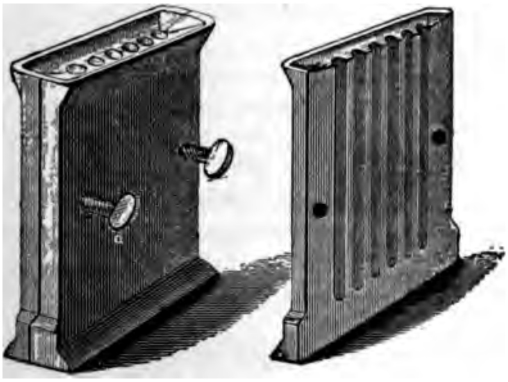
Preparation.—Potassium hydrate is prepared by slaking 3 parts of calcium oxide with a small quantity of water, and then rubbing to a fine powder with 10 parts of water. This is added in small portions at a time to 4 parts of potassium carbonate, previously dissolved in 15 to 20 parts of water. The mixture is then heated to the boiling point for twenty minutes, the heat removed, and the vessel closely covered until the liquid has settled clear. Water must be added from time to time during the heating, for if the solution become too concentrated a reverse reaction sets in. The operation is known to be complete when a portion of the clear solution gives no effervescence on supersaturating with an acid. The reaction which takes place in the formation of the hydrate is as follows:

$$\underset{\text{Potassium Carbonate.}}{K_2CO_3} + \underset{\text{Calcium Hydrate.}}{Ca(OH)_2} = \underset{\text{Potassium Hydrate.}}{2KOH} + \underset{\text{Calcium Carbonate.}}{CaCO_3}.$$

The clear liquid is removed from the sediment by a siphon, and evaporated in an iron dish to a specific gravity of 1.16, when it begins to attack the iron, and further concentration must be conducted in a silver vessel.

When the liquid has assumed an oily consistence, and a drop removed on a glass rod solidifies on cooling, it is poured into silver moulds. The moulds are illustrated in Fig. 60. In order to obtain a product free from aluminum hydrate, sulphates and chlorides, 1 part of the potassium hydrate is dissolved in 3 to 4

FIG. 60.



Moulds for potassium hydrate.

parts of highly rectified alcohol, the clear liquid decanted from the sediment, boiled down in a silver dish, and cast in moulds as before. A still purer potassium hydrate is sometimes prepared by dissolving metallic potassium in water.

Properties.—Potassium hydrate, when pure, is a white, crystalline, brittle solid. It is odorless, and has a sharp, caustic taste, and an alkaline reaction. It is soluble in 0.5 part of water at 15°, and in 2 parts of alcohol; it is very soluble in boiling water and in boiling alcohol. When heated to a temperature of 530°, it melts to a clear oily liquid, and at a bright red heat it is volatilized unchanged. It absorbs carbon dioxide and water from the air, and dissolves in the latter with evolution of heat. When the concentrated aqueous solution is cooled, a compound containing two molecules of water, $KOH.2H_2O$, crystallizes out in tabular or octohedral crystals. The solution in alcohol rapidly assumes a dark-yellow to brown color, and in the presence of air there are formed acetic acid, aldehyde, and aldehyde resin.

The **Liquor Potassæ** of the Pharmacopœia contains about 5 per cent. of the hydrate, and has a specific gravity of about 1.036. The official process directs that this solution be made from potassium bicarbonate and lime, since the bicarbonate is found purer in commerce than the normal carbonate.

The commercial caustic potash usually contains from 75 to 90 per cent. of absolute potassium hydrate, and 10 to 25 per cent. of water.

OXYGEN SALTS OF POTASSIUM AND THE HALOGENS

Potassium Hypochlorite, $KClO$, is known only in solution. It is the active ingredient in "Eau de Javelle," which is prepared by passing chlorine into cold dilute solution of potassium carbonate or hydrate The result is a solution of potassium hypochlorite and chloride. Thi solution was formerly much used for bleaching purposes.

Potassium Chlorate, $KClO_3$. **Potassii Chloras,** U. S. P.— This salt was discovered and first prepared by Berthollet in 178

Preparation.—The simplest method of preparing potassiu chlorate on a small scale is by passing chlorine into a strong, h solution of potassium hydrate:

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$$

Owing to the formation at the same time of a considerab quantity of potassium chloride, this is rather an expensive proce and on a commercial scale other methods have been introduce

The commercial production of potassium chlorate is accomplished by treating milk of lime with an excess of chlorine in a vessel in which the mixture is constantly agitated. The result is calcium chlorate and chloride, as follows:

$6Ca(OH)_2$	$+$	$6Cl_2$	$=$	$5CaCl_2$	$+$	$Ca(ClO_3)_2$	$+$	$6H_2O$.
Calcium Hydrate.		Chlorine.		Calcium Chloride.		Calcium Chlorate.		Water.

After allowing the mixture to settle, the clear liquid is drawn off and evaporated with potassium chloride to a specific gravity of 1.28, when the following reaction takes place between the calcium chlorate and the potassium chloride:

$$Ca(ClO_3)_2 + 2KCl = 2KClO_3 + CaCl_2.$$

The potassium chlorate, being rather insoluble in water, crystallizes out, and, after separation, it is purified by dissolving in hot water and recrystallizing.

It has been proposed to use magnesium oxide suspended in water instead of milk of lime, on account of the resulting magnesium chloride having less solvent action on the potassium chlorate than is possessed by the calcium chloride.

Another commercial process consists in mixing solutions of potassium chloride and calcium hypochlorite (bleaching powder). The whole is then cooled, when potassium chlorate separates out:

$2KCl$	$+$	$3(Ca(OCl)_2 + CaCl_2)$	$=$	$2KClO_3$	$+$	$6CaCl_2$.
Potassium Chloride.		Calcium Hypochlorite.		Potassium Chlorate.		Calcium Chloride.

Properties.—Potassium chlorate occurs in "colorless, lustrous, monoclinic prisms or plates, or a white powder, odorless, and having a cooling, saline taste. Permanent in the air. Soluble in 16.7 parts of water at 15°, and in 1.7 parts of boiling water; insoluble in absolute alcohol, and but slightly soluble in mixtures of alcohol and water."

When heated to 334° the salt melts, and at 352° it commences to decompose into oxygen, potassium chloride and perchlorate. At about 400° the perchlorate is decomposed, with further evolution of oxygen, potassium chloride only remaining. This residue should amount to 60.8 per cent. of the original weight, should be completely soluble in water, and the resulting aqueous solution should form a white, crystalline precipitate with a saturated solution of sodium bitartrate.

Uses.—One of the principal uses of potassium chlorate is in the preparation of oxygen on a small scale. It is also largely employed as an oxidizing agent in calico-printing. In the manufacture of colored fires this salt plays an important part. It has considerable use in medicine, especially in diseases of the throat. In large doses it acts as an irritant poison.

Potassium chlorate should never be ground or rubbed with organic substances or with sulphur, as violent explosions are almost sure to occur. In case it is necessary to make such mixtures, the ingredients should be powdered separately, and then carefully mixed without friction. These mixtures should not be preserved, as spontaneous decomposition takes place, resulting either in combustion or explosion.

Mixtures of potassium chlorate and ammonium chloride have exploded violently after standing for some time.

Colored fires are made by taking 25 to 50 parts of potassium chlorate and 25 parts of powdered sugar or shellac as a base; to this mixture are added 25 parts of strontium nitrate for red, 25 parts of barium nitrate for green, 10 parts of copper nitrate for blue, and 10 parts of sodium nitrate or chloride for yellow. Sulphur may be used in place of sugar or shellac, but the resulting powder is more liable to decompose with combustion or explosion.

Potassium Perchlorate, $KClO_4$, is prepared by heating potassium chlorate to 352°, when it is decomposed into perchlorate, chloride, and oxygen; the oxygen escapes, and the two salts remain behind as a pasty mass.

This is cooled, powdered, and treated with cold water, which removes the potassium chloride. The undissolved residue is digested with warm hydrochloric acid to decompose chlorate and convert it into chloride, which is then washed out with cold water. The residue consists of nearly pure perchlorate, which may be further purified by recrystallization from hot water.

The perchlorate is one of the most insoluble of potassium salts, requiring 65 parts of cold and 5.04 parts of boiling water to dissolve it. It is practically insoluble in alcohol. At 400° it is decomposed into potassium chloride and oxygen.

Potassium Bromate, $KBrO_3$.—When bromine is added to potassium hydrate, the following reaction takes place:

$$6KOH + 3Br_2 = KBrO_3 + 5KBr + 3H_2O.$$

It may be more economical to pass chlorine into a hot solution of potassium bromide and hydrate, as follows:

$$KBr + 6KOH + 3Cl_2 = KBrO_3 + 6KCl + 3H_2O.$$

The bromate partly crystallizes out on cooling. On concentrating further, more of the bromate crystallizes out mixed with some chloride, from which, however, it is readily purified by recrystallization from hot water.

Another convenient method of preparation is to decompose barium bromate with potassium sulphate; the mixture is heated to the boiling point, the insoluble barium sulphate is removed by filtration from the solution of potassium bromate, and the latter allowed to cool and crystallize. The salt occurs in six-sided plates or prisms, and is quite insoluble in cold water.

Potassium Iodate, KIO_3.—When chlorine is passed into cold water holding iodine in suspension, until the latter disappears, iodine monochloride, ICl, is formed; to this is added the molecular proportion of potassium chlorate and the mixture warmed, when chlorine is evolved and potassium iodate separates out in cubical crystals:

$$ICl + KClO_3 = KIO_3 + Cl_2.$$

The salt is soluble in 13 parts of cold water, and decomposes, when strongly heated, into potassium iodide and oxygen.

Potassium Periodate, KIO_4, is prepared by passing chlorine into a mixture of potassium iodate and hydrate. The salt separates out in small rhombic crystals, and requires 300 parts of cold water for solution. Between 250° and 300° it decomposes into potassium iodate and oxygen, and at a higher temperature it parts with all of its oxygen, leaving a residue of potassium iodide.

POTASSIUM AND SULPHUR.

Potassium monosulphide, K_2S.
Potassium disulphide, K_2S_2.
Potassium trisulphide, K_2S_3.
Potassium tetrasulphide, K_2S_4.
Potassium pentasulphide, K_2S_5.
Potassium hydrosulphide, KSH.

Potassium Monosulphide, K_2S, is prepared by heating to redness in a well-covered vessel an intimate mixture of 7 parts of potassium sulphate and 2 parts of finely-powdered charcoal, when the following reaction takes place:

$$K_2SO_4 + 4C = K_2S + 4CO.$$

The same compound is obtained when one volume of potassium hydrate solution is saturated with hydrogen sulphide, and then mixed with an equal volume of the same strength potassium hydrate solution:

$$KOH + H_2S = KSH + H_2O.$$
$$KSH + KOH = K_2S + H_2O.$$

Properties.—When potassium monosulphide is treated with a small proportion of water, it dissolves unchanged, and will crystallize from its solution with 5 molecules of water. When, however, it is treated with a larger quantity of water, it decomposes into the hydrosulphide and hydrate, as follows:

$$K_2S + H_2O = KSH + KOH.$$

On the application of heat it melts to a black liquid, which cools to a reddish, crystalline mass.

Potassium Hydrosulphide, KSH, is formed when hydrogen sulphide is passed into a solution of potassium hydrate; by evaporating this solution in a vacuum, crystals are formed containing 1½ molecules of water.

The remaining potassium sulphides may be appropriately termed polysulphides, and may be formed by heating the monosulphide with the molecular proportion of sulphur, observing at the same time the proper degree of heat.

Potassa Sulphurata, U. S. P., is a mixture of polysulphides with potassium sulphate and thiosulphate. It is prepared by fusing together sulphur and potassium carbonate.

"When freshly prepared, sulphurated potassa forms irregular pieces of a liver-brown color, which, by exposure to the air, gradually absorb moisture, oxygen, and carbon dioxide, and change to a greenish-yellow, and finally to a gray mass containing potassium carbonate, hyposulphite, and sulphate.

"Soluble in 2 parts of water at 15°, with the exception of a small residue. Alcohol dissolves only the potassium sulphide, leaving the other constituents (hyposulphite and sulphate) undissolved."

OXYGEN SALTS OF POTASSIUM AND SULPHUR.

Potassium Sulphite, $K_2SO_3.2H_2O$.—The salt of this formula is the normal potassium sulphite. It is prepared by passing sulphur dioxide into a solution of potassium carbonate, until the mixture reacts strongly acid:

$$K_2CO_3 + 2SO_2 + H_2O = 2KHSO_3 + CO_2.$$

To this solution potassium carbonate is added to a neutral or faint alkaline reaction. The slight excess of sulphur dioxide forms the ac sulphite, which, on the addition of the carbonate, is converted into ne tral or normal sulphite, as follows:

$$2KHSO_3 + K_2CO_3 = 2K_2SO_3 + CO_2 + H_2O.$$

The solution is concentrated without much heat, and monoclinic oct hedral crystals separate out.

Potassium sulphite is somewhat deliquescent, odorless, and has a bitte saline, sulphurous taste. It has a neutral or feebly alkaline reaction. is more soluble in cold than in hot water, requiring 4 parts of water 15° and 5 parts of boiling water for solution, alcohol has very slig solvent action. On the application of heat, the salt loses its water crystallization, amounting to 18.5 per cent. At a higher temperatu decomposition takes place, with the formation of potassium sulpha sulphite, and hydrate, the residue, therefore, has an alkaline reactio

Acid Potassium Sulphite, $KHSO_3$, is prepared from potassium bonate and sulphur dioxide. according to the equation given under normal sulphite. It forms in monoclinic prisms, but by adding alcohol to the concentrated aqueous solution, it may be obtained in acicular crystals. The salt is very soluble in water, has a neutral or slightly alkaline reaction, and emits the odor of sulphur dioxide. On exposure to air it gradually changes to sulphate.

Potassium Disulphite, or Pyrosulphite, $K_2S_2O_5$, is formed when sulphur dioxide is passed into a hot saturated solution of potassium carbonate until effervescence ceases and the liquid assumes a greenish tinge. On cooling, the salt separates in granular crystals. It is difficultly soluble in water, and has an acid, disagreeable taste.

Potassium Sulphate, K_2SO_4. **Potassii Sulphas, U. S. P.**—This salt has been known since the fourteenth century. It occurs in many mineral waters, in sea water, and in the ashes of many plants. The chief locality of its occurrence is in the Stassfurt salt-beds. Kainite is a double sulphate of potassium and magnesium with magnesium chloride, $K_2SO_4MgSO_4MgCl_2.5H_2O$; schoenite is a double sulphate of potassium and magnesium, $K_2SO_42MgSO_4.6H_2O$.

These two minerals form the chief sources of the salt. It may be obtained as a by-product in the manufacture of nitric acid from potassium nitrate and sulphuric acid, in the manufacture of potassium bichromate, in the decomposition of potassium tartrate by calcium sulphate, in the manufacture of sulphuric acid, and in the manufacture of potassium carbonate from potassium chloride in the Leblanc process.

Preparation.—In the preparation of the salt from kainite, the mineral is exposed to the air until the more soluble magnesium chloride deliquesces and runs off. The remaining salt is dissolved in boiling water, which decomposes it, and, on cooling, the less soluble potassium sulphate crystallizes first.

Properties.—Potassium sulphate occurs in "hard, colorless, transparent, six-sided, rhombic prisms terminated by pyramids, or a white powder, odorless, and having a somewhat bitter, saline taste. Permanent in the air. Soluble in about 9.5 parts of water at 15°, and in 4 parts of boiling water; insoluble in alcohol. When heated, the crystals decrepitate. At a bright red heat they fuse, and at a white heat the salt suffers partial decomposition. The aqueous solution is neutral to litmus paper." The specific gravity of the crystals is 2.648.

Potassium sulphate has some uses in medicine, and it is extensively employed in the preparation of potash alum and potassium carbonate.

Acid Potassium Sulphate (Potassium Bisulphate), $KHSO_4$.—This salt is found native in the Grotto del Sofo, near Naples, in the form of long acicular crystals. Its usual source and method of preparation are from the residue of the manufacture of nitric acid from potassium nitrate when an excess of sulphuric acid has been used.

When the salt is separated from an acid solution, it is obtained in the form of tabular rhombic crystals, which are easily soluble in water. From dilute solutions of the acid sulphate the neutral sulphate crystallizes; following this, as the solution is concentrated, there separates a salt having the composition $K_2SO_4KHSO_4$, and then the acid salt crystallizes. From this it appears that in dilute solution the acid salt is dissociated into neutral potassium sulphate and sulphuric acid. This is also observed when the acid salt is mixed with alcohol: a decomposition takes place, the neutral sulphate separates, while the sulphuric acid passes into solution in the alcohol.

Acid potassium sulphate fuses at 200°, and above that temperature is converted into *potassium pyrosulphate*, $K_2S_2O_7$. This salt at a temperature of 600° decomposes into neutral sulphate and sulphur trioxide.

Potassium pyrosulphate crystallizes in long needles, and when brought in contact with water evolves much heat and is converted into the acid sulphate.

Acid Potassium Disulphate, KHS_2O_7, is formed when the pyrosulphate is dissolved in fuming sulphuric acid, and from this liquid it is deposited in transparent prismatic crystals.

Acid potassium sulphate is useful as a flux, because in this way it is possible to bring sulphuric acid in contact with many bodies at a temperature considerably above its boiling point.

OXYGEN SALTS OF POTASSIUM AND NITROGEN.

Potassium Nitrate (Saltpetre, Nitre), KNO_3. **Potassii Nitras**, U. S. P.—Saltpetre was known in the eighth century. It is very widely distributed in nature, mixed more or less with other salts, chiefly calcium nitrate. It is found most abundantly in the warm climates of India, Egypt, Hungary, and South America. Formerly most of the salt came from India. It is made there by collecting the efflorescence from stables and other places where nitrogenous matter is undergoing decomposition with free access of air. This efflorescence is obtained from large heaps of manure, on which urine is poured daily. As the surface dries and shows the presence of the salt, it is removed, and this process repeated until the bed, after two or three years, become exhausted. The crude liquors are treated with potassium carbonate, which precipitates the calcium, and the clear liquid is separated and concentrated to crystallize.

The greatest production of the salt now is from Chili saltpetre, sodium nitrate, by double decomposition with potassium chloride, as follows:

$NaNO_3$	+	KCl	=	KNO_3	+	$NaCl$.
Sodium Nitrate.		Potassium Chloride.		Potassium Nitrate.		Sodium Chloride.

The hot saturated solutions of these two salts are mixed and concentrated until the solution reaches a specific gravity of 1.5, when the sodium chloride, being no more soluble in hot than in cold water, separates out and is removed. The liquid is then drawn off and allowed to cool, when the potassium nitrate crystallizes in fine powder. This is removed and washed with a small quantity of cold water, which removes the last of the sodium chloride. The salt is then purified by recrystallization.

In order more fully to explain this method of preparing the salt, the following solubilities are given:

	15°.	100°.
100 parts of water dissolve KNO_3 .	26 parts.	247 parts.
100 parts of water dissolve $NaNO_3$.	86.3 "	168.2 "
100 parts of water dissolve KCl . .	33.4 "	56.6 "
100 parts of water dissolve $NaCl$.	36 "	39.2 "

Properties.—Potassium nitrate occurs in "colorless, transparent, six-sided, rhombic prisms, or a crystalline powder, odorless, and having a cooling, saline, and pungent taste. Permanent in the air. Soluble in 3.8 parts of water at 15°, and in 0.4 part of boiling water; very sparingly soluble in alcohol. When heated to 353°, the salt melts. At a higher temperature it is decomposed, giving off oxygen at first, and then some of its nitrogen, leaving a residue of potassium nitrate, nitrite, and oxide. Thrown on red-hot coals, the salt deflagrates. The aqueous solution is neutral to litmus paper."

Uses.—Potassium nitrate is used in medicine and as a preservative; in the latter capacity it enters into the composition of most of the meat preservatives, boric acid, borax, and sodium carbonate being the other compounds usually associated with it. The chief use of potassium nitrate is in the manufacture of gunpowder. The average composition of gunpowder is as follows:

Potassium nitrate	74.9 parts.
Charcoal	13.3 "
Sulphur	11.8 "
	100.00 "

In actual practice the composition varies somewhat from the above, since charcoal is not a uniform substance, consequently the character of the charcoal used in each case must be taken into account. The amount of the constituents is also varied according to the purposes to which the powder is to be applied.

Potassium Nitrite, KNO_2.—This salt is usually prepared by fusing in an iron vessel 1 part of potassium nitrate, to which are then added, in small portions at a time, 2 parts of powdered metallic lead; the latter is rapidly oxidized, as follows:

$$KNO_3 + Pb = KNO_2 + PbO.$$

On cooling, the mass is treated with water, and from the solution of the potassium nitrite any lead is removed by carbon dioxide. The solution is then concentrated to a small bulk and the undecomposed nitrate allowed to crystallize out. The clear solution of now nearly pure nitrite is next evaporated to dryness, which yields the salt in masses of small, indistinct crystals. It is deliquescent in moist air, but nearly insoluble in alcohol. It usually comes in commerce in sticks of a yellowish color.

OXYGEN SALTS OF POTASSIUM AND PHOSPHORUS.

There are three potassium salts of orthophosphoric acid.

Tripotassium Orthophosphate, K_3PO_4, is prepared by heating to redness phosphoric acid and potassium carbonate or hydrate. It is readily soluble in water, and separates in small, colorless, acicular crystals.

Dipotassium Orthophosphate, K_2HPO_4.—This salt is formed when orthophosphoric acid is neutralized with potassium carbonate. The resulting compound is difficult to crystallize.

Monopotassium Orthophosphate, KH_2PO_4, is produced when the above dipotassium compound is heated with an excess of orthophosphoric acid. It usually separates in large, colorless, rhombic crystals.

There are two potassium salts of pyrophosphoric acid, according as two or four atoms of hydrogen are replaced by the base.

Potassium Pyrophosphate, $K_4P_2O_7$, is obtained by neutralizing pyrophosphoric acid with potassium hydrate, or, perhaps, more conveniently by heating the dipotassium orthophosphate to redness. It is a deliquescent salt which separates from solution in fibrous crystals, containing three molecules of water.

Dipotassium Pyrophosphate, $K_2H_2P_2O_7$.—This is the acid salt, and is prepared by dissolving the neutral salt in acetic acid and precipitating with alcohol.

Potassium Metaphosphate, KPO_3, is prepared by heating the monopotassium orthophosphate to redness. As thus obtained it is in translucent masses, nearly insoluble in water, but readily soluble in dilute acids. Although monobasic, metaphosphoric acid possesses the property of polymerization, so that there are at least five compounds of potassium with the acid, having the following formulas: KPO_3, metaphosphate; $K_2P_2O_6$, dimetaphosphate; $K_3P_3O_9$, trimetaphosphate, etc.

Potassium Hypophosphite, KH_2PO_2. **Potassii Hypophosphis, U. S. P.**—This salt is prepared by decomposing calcium hypophosphite with potassium carbonate, as follows:

$Ca(H_2PO_2)_2$	+	K_2CO_3	=	$2KH_2PO_2$	+	$CaCO_3$.
Calcium Hypophosphite.		Potassium Carbonate.		Potassium Hypophosphite.		Calcium Carbonate.

The details of the process are to add 5.75 parts of potassium carbonate, in 8 parts of water, to 6 parts of calcium hypophosphite, in 64 parts of water; allow to stand until the precipitate settles, filter, and evaporate the filtrate at a temperature not exceeding 100° until granulation is effected. By failing to keep below the temperature specified an explosion is liable to occur. The product is purified by dissolving in alcohol, evaporating to a syrupy consistence, and crystallizing.

Potassium hypophosphite occurs in "white, opaque, hexagonal plates, or crystalline masses, or a granular powder, odorless, and having a pungent, saline taste; very deliquescent. Soluble, at 15°, in 0.6 part of water, and in 7.3 parts of alcohol; in 0.3 part of boiling water, and in 3.6 parts of boiling alcohol; insoluble in ether. When heated in a dry test-tube, the salt at first loses moisture, and then evolves spontaneously inflammable hydrogen phosphide gas, which burns with a bright yellow flame."

This salt should not be rubbed with nitrates, chlorates, permanganates, or other oxidizing agents, as, under these circumstances, it will explode violently.

OXYGEN SALTS OF POTASSIUM AND BORON.

Potassium Metaborate, KBO_2, is formed when molecular weights of boric oxide and potassium carbonate are fused together. The product is soluble in water and crystallizes with difficulty.

There are several other borates, the most important of which is the tetraborate, $K_2B_4O_7.5H_2O$. It is prepared by adding potassium hydrate to a solution of boric acid until an alkaline reaction is obtained. This compound resembles the corresponding sodium salt, which will be treated more fully.

OXYGEN SALTS OF POTASSIUM AND SILICON.

Potassium Silicate, K_2SiO_3, is produced when amorphous silica or silicic acid is dissolved in potassium hydrate. It is also formed when silica is fused with potassium carbonate. It occurs in amorphous vitreous masses, which readily deliquesce when exposed to the air and gradually become converted into a transparent jelly, which then shrinks to a hard mass.

Potassium Tetrasilicate, $K_2Si_4O_9$.—This is the soluble potash glass. It is prepared by fusing together 45 parts of quartz with 30 parts of potassium carbonate and 3 parts of charcoal. The fused mass is dissolved in 5 times its weight of boiling water and concentrated to the desired strength.

Potassium Fluosilicate, K_2SiF_6, is prepared by precipitating any salt of potassium with hydrofluosilicic acid. The resulting compound is quite insoluble in cold water, but readily dissolves in that solvent when hot.

OXYGEN SALTS OF POTASSIUM AND CARBON.

Potassium Carbonate, K_2CO_3.—The more or less pure carbonates of potassium are known as *potash*, *pearlash*, and *salt of tartar*, according to their degree of purity.

Source.—The chief sources of potassium carbonate are: (1) Wood-ashes, (2) beet-root molasses, (3) sheep's wool, and (4) potassium chloride and sulphate.

(1) Wood-ashes. All land plants contain potassium salts, and these, when the plants are burned, are almost entirely converted into carbonate. Russia, America, and Hungary, on account of their plentiful supply of timber, furnish most of the carbonate from this source.

The following are some of the percentages of potassium yielded by different woods:

Pine	0.045	Oak	0.153
Poplar	0.075	Willow	0.285
Beech	0.145	Elm	0.390

In America much lye (a solution of potassium carbonate and hydrate) is made in a small way by those who use wood for fuel. The apparatus in which this is accomplished consists of a square wooden hopper or percolator of two or three hundred pounds capacity, in the bottom of which is placed a layer of straw, then a layer of quick-lime, and then alternate layers of ashes and quick-lime to the top, the last layer being a thick one of ashes. Water is poured on in small quantities at a time for a week or so, and the resulting solution, which is collected underneath, consisting of potassium carbonate and hydrate, is used for the manufacture of soft soap.

On the large scale the lixiviation is carried out the same as that described above, except that the use of lime appears to be confined to America. Wood is usually the material employed for procuring the carbonate, although in Eastern Russia grass, the green portions of potatoes, and other vegetables are burned for their ash.

For commercial purposes the solution resulting from the lixivi ation of the ashes is evaporated to dryness in iron pans, and the dark-brown product contains from 6 to 12 per cent. of water. The color, which is due to organic matter, is removed by heating the salt to about 800° ; the mass at first blackens, but slowly becomes white, when the heat is removed, the salt cooled, and packed immediately in air-tight casks.

Russian potash is said to contain from 50 to 60 per cent. of potassium carbonate and some hydrate. The American product is usually purified by solution in water, re-evaporated and ignited, when it contains from 75 to 90 per cent. of absolute carbonate ; it is then known as pearlash. Most of the potash in the market contains more or less sulphate, sometimes as much as 18 per cent. During the concentration of the lye liquor the sulphate crystallizes out. Formerly this was raked out and used in the manufacture of alum.

The American potash is chiefly produced in Canada. In 1892, 1,409,200 pounds passed under observation of the government at Montreal. Birch and maple are the chief wood there consumed in this industry.

(2) When the molasses from beet-root sugar is allowed to ferment, and is then distilled, there remains a residue which contains 30 to 35 per cent. of potassium carbonate, 18 to 20 per cent. sodium carbonate, and smaller amounts of chlorides, sulphates, and insoluble matter ; this residue is calcined, dissolved in a small quantity of water, and the clear solution again evaporated and calcined, whereby the percentage of potassium carbonate is increased to an amount that warrants its use as pearlash.

(3) Sheep's wool contains a relatively large amount of potassium combined with some inorganic acids, but chiefly with the stearic, oleic, palmitic, and benzoic acids.

When the wool is washed these compounds go into solution, and, on evaporation and ignition, the residue is found to contain about 30 per cent. of potassium carbonate. The processes of solution, evaporation, and ignition are repeated, whereby the percentage of potassium carbonate is raised, and the product becomes purer.

(4) Potassium chloride and sulphate, occurring native as minerals at Stassfurt, Germany, are, perhaps, the greatest sources of potassium carbonate at the present time. By a process similar to that of Leblanc, used in the preparation of sodium carbonate, these minerals are converted into a very pure carbonate. In

[illegible]

[illegible]

[illegible] the latter [illegible] porous [illegible] running through the [illegible]. When the [illegible], heat is applied for some time in order to dissipate small quantities of cyanogen and ammonium compound. The residue is dissolved in a small quantity of water, filtered, evaporated, and granulated. The operation in this case should be conducted in a silver dish. The product retains the name of *salt of tartar* to the present time, indicating the source from which it was at one time exclusively obtained. The pure salt may also be made by heating crystallized potassium bicarbonate; as this salt is capable by crystallization of being prepared of a high degree of purity, a superior product may thus be obtained.

$$2KHCO_3 = K_2CO_3 + CO_2 + H_2O.$$

[illegible] Water.

Properties.—[illegible] white, dry, granular powder, [illegible] strongly alkaline taste.

It is very deliquescent, absorbing moisture readily from the air; soluble in 1.1 parts of water at 15°, and in 0.65 part of boiling water: insoluble in alcohol. On heating to 130°, the salt loses the adhering moisture, which should not be more than 5 to 8 per cent., and at a red heat it melts, slowly volatilizing as the heat is increased to whiteness. The solution of the salt reacts strongly alkaline to litmus, and effervesces with acids.

From the concentrated aqueous solution crystals separate, having the formula $K_2CO_3.3H_2O$.

Potassium Bicarbonate, $KHCO_3$. **Potassii Bicarbonas, U.S.P.**—On passing carbon dioxide into a concentrated solution of the normal carbonate, the acid carbonate crystallizes out according to the following reaction:

$$K_2CO_3 + CO_2 + H_2O = 2KHCO_3.$$

The same result is sometimes accomplished by passing the carbon dioxide over the moistened pearlash. The product by either process is dissolved in water, filtered clear, and allowed to crystallize.

Properties.—Potassium bicarbonate occurs in colorless, transparent, monoclinic prisms. It is without odor, and has a saline and slightly alkaline taste. It is soluble in 3.2 parts of water at 15°, and in 1.9 parts at 50°. Above that temperature, in aqueous solution, it is rapidly decomposed into normal carbonate and carbon dioxide. It is insoluble in alcohol. When first dissolved in water the resulting solution has a neutral reaction, but on standing it becomes alkaline owing to the formation of the normal carbonate.

POTASSIUM AND CYANOGEN.

Potassium Cyanide, KCN.—This salt is prepared by taking an intimate mixture of 8 parts potassium ferrocyanide and 3 parts potassium carbonate, and projecting in small portions at a time into a red-hot iron crucible, when the following reaction takes place:

$$\underset{\substack{\text{Potassium}\\\text{Ferrocyanide.}}}{K_4Fe(CN)_6} + \underset{\substack{\text{Potassium}\\\text{Carbonate.}}}{K_2CO_3} = \underset{\substack{\text{Potassium}\\\text{Cyanide.}}}{5KCN} + \underset{\substack{\text{Potassium}\\\text{Cyanate.}}}{KOCN} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{CO_2} + \underset{\text{Iron.}}{Fe.}$$

When effervescence has ceased, and the liquid has become clear, it is poured carefully into an iron dish to solidify.

The French process, which, it is claimed, will yield a purer product, consists in heating the potassium ferrocyanide alone with exclusion of air to a bright red heat:

$$\underset{\text{Potassium Ferrocyanide.}}{K_4Fe(CN)_6} = \underset{\text{Potassium Cyanide.}}{4KCN} + \underset{\text{Iron Carbide.}}{FeC_2} + \underset{\text{Nitrogen.}}{N_2}$$

A portion of the melted mass can be poured off clear, and the black residue can be extracted with alcohol.

A chemically pure potassium cyanide is prepared by passing hydrocyanic acid gas into an alcoholic solution of potassium hydrate. The salt separates out as a white, crystalline powder.

Properties.—Potassium cyanide occurs either in white, amorphous, opaque pieces, or as a white, granular powder. It may be obtained in regular octohedrons by allowing the concentrated aqueous solution to evaporate over sulphuric acid at ordinary temperatures. When perfectly dry it is odorless, but as ordinarily found it has an odor of hydrocyanic acid, owing to the presence of moisture. Its taste is sharp, bitterish, and somewhat alkaline. The salt is soluble in 2 parts of water at 15°, and in an equal weight of boiling water; at the latter temperature, however, it is rapidly decomposed. It is sparingly soluble in alcohol. When exposed to damp air, the salt readily deliquesces. The aqueous solution has an alkaline reaction. When heated to low redness, the salt fuses, and, on cooling, solidifies in cubes. It is decomposed by the weakest acids, even carbonic acid being able to displace the hydrocyanic radical. Violent explosions occur when this salt is mixed with nitric acid or with potassium chlorate. Potassium cyanide is official under the name of **Potassii Cyanidum.** Its use in medicine is limited. In electro-metallurgy and in photography it is more extensively employed.

Potassium Cyanate, KCNO.—When equal parts of potassium ferrocyanide and manganese dioxide are intimately mixed, and fused until the mass begins to soften, potassium cyanate is formed. After allowing the mass to cool it is extracted with 80 per cent. alcohol, and this solvent, on cooling, deposits the salt in transparent tabular crystals. It is readily soluble in water and in alcohol. The salt in aqueous solution gradually decomposes into water and potassium bicarbonate. It is chiefly used in the preparation of organic compounds.

Potassium Thiocyanate, or Sulphocyanate, KCNS.—This salt is prepared by gently heating together 46 parts of potassium ferrocyanide, parts of potassium carbonate, and 32 parts of sulphur. When the fused mass is cooled it is extracted with hot alcohol, and this solvent deposits the crystallized salt, on cooling, in long striated transparent prisms.

Potassium thiocyanate is very soluble in water and in alcohol. On account of the deep red color it produces with ferric salts, it becomes delicate test for them.

SODIUM.

Symbol, Na. *Atomic Weight,* 23. *Valence,* I.

History.—As stated under the preceding element, the salts of sodium and potassium were not distinguished from each other until 1736. Those of sodium were probably the first known. *Nitrum,* which later came to be a name for saltpetre, was probably in earlier times applied to an impure sodium carbonate, since it effervesced on the application of vinegar. Sodium chloride, because of its presence in sea water, was known in the earliest times.

The metal sodium was discovered by Davy in 1807, in the same manner as potassium,—namely, by the electrolysis of the hydrate.

Occurrence.—Sodium, like the other alkali metals, is not found in nature in the free state; but in combination it is very widely distributed. Sodium chloride is found as rock-salt in the earth, it is a constituent of sea water, of the water of many mineral springs, and it is almost universally distributed in animal and vegetable organisms.

Sodium silicate is a constituent of albite, or soda-feldspar, and in smaller quantity in many other minerals. The nitrate, as Chili saltpetre, is found in the warm and rainless districts of Chili and Peru. Cryolite, found in large deposits in Greenland, is the double fluoride of sodium and aluminum. Sodium carbonate occurs as a natural deposit in the warm and rainless districts of many countries, notably in Egypt, India, South America, and in Wyoming and California; in the latter places, however, it is usually associated with larger quantities of sodium sulphate or borate. Smaller quantities of the sulphate and the iodide are found in sea water.

Preparation.—Sodium is produced by the electrolytic apparatus of Castner, described under potassium, Fig. 59. It is also manufactured on a large scale by a process of Castner, in which sodium hydrate and iron carbide are heated together to 800°, when sodium distils according to the following reaction:

$$\underset{\substack{\text{Sodium}\\ \text{Hydrate.}}}{6NaOH} + \underset{\substack{\text{Iron}\\ \text{Carbide.}}}{FeC_2} = \underset{\substack{\text{Sodium}\\ \text{Carbonate.}}}{2Na_2CO_3} + \underset{\text{Hydrogen.}}{3H_2} + \underset{\text{Iron.}}{Fe} + \underset{\text{Sodium.}}{Na_2}.$$

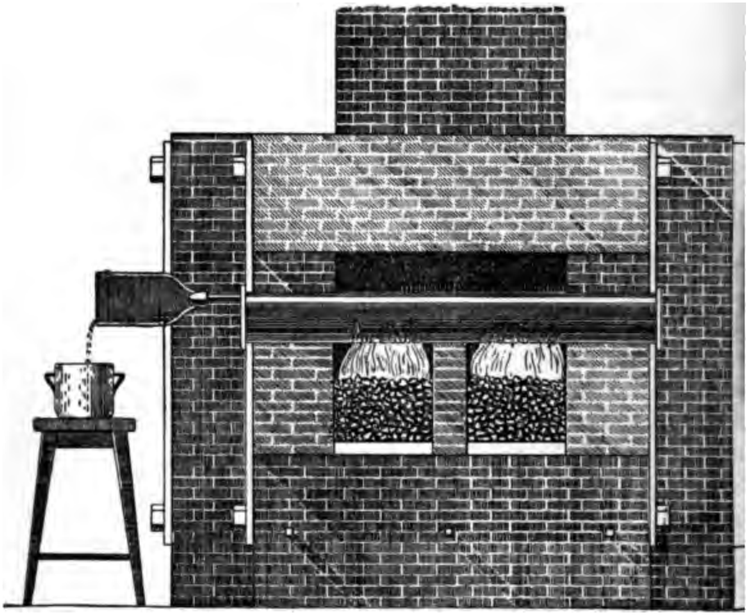
The operation is most successful when the ingredients are very intimately mixed.

The older method of Deville is still used considerably. This consists in heating an intimate mixture of sodium carbonate and carbon, when the following reaction occurs:

$$Na_2CO_3 + 2C = Na_2 + 3CO.$$

The apparatus by which this is accomplished is shown in Fig. 61. A charge for this apparatus consists of 30 kilogrammes of soda-ash, ground with 13 kilogrammes of small coal and 3 kilogrammes of chalk. This is placed in the cylinder A, which is 1.2 meters long and 0.14 meter in diameter, and the whole i brought to a white heat. There is not the same danger from explosion that there is in the preparation of metallic potassiu Much sodium is lost during the operation, the yield being abo one-third of the theoretical amount present.

FIG. 61.



Sodium furnace.

It has also been proposed to prepare sodium by electrolys directly from the chloride, since both the metal and the chlori are valuable; many suggestions have been made and a numb of patents granted, but as yet the process does not appear to ha become a success.

Properties.—Sodium is a silver-white metal, of a waxy consistence at ordinary temperatures, but in the cold it becomes brittle and crystalline. It has a specific gravity of 0.9735 at 13.5°.

On the application of heat sodium melts at 95.6°, and at 742° it boils; under these conditions it is necessary to exclude air. The metal is so easily oxidized at ordinary temperatures that it is necessary to preserve it under petroleum. If it is melted in the atmosphere of an inert gas like nitrogen, and when it begins to solidify the liquid portion is poured out, the remainder takes the form of octohedral crystals.

The behavior of sodium towards most other elements is similar to that of potassium, but less energetic; for instance, potassium and bromine combine with explosive violence, while sodium may be warmed with it without violent action.

When thrown on water, sodium combines with the oxygen of the water, liberating hydrogen, but the action is not sufficiently energetic to inflame the latter, unless the metal be held in one position by a piece of filter paper, or the water be warmed to 60°, when the gas ignites and burns with a yellow flame. This yellow color is characteristic of sodium compounds.

Uses.—Sodium is used in the preparation of a number of other metals, notably, silicon, boron, magnesium, and aluminum. It is also a valuable reducing agent in the laboratory. In some cases where its activity does not admit of its being used alone, as in aqueous solutions, it is first amalgamated with mercury.

SODIUM AND HYDROGEN.

Sodium Hydride, Na_4H_2.—When dry hydrogen is passed over sodium at a temperature of 300° to 400° the metal absorbs 237 times its volume of the gas. The product has a silver-white color, and a metallic lustre. Its specific gravity is 0.959.

SODIUM AND HALOGENS.

The halogen compounds of sodium are:

Sodium fluoride, NaF.
Sodium chloride, $NaCl$.
Sodium bromide, $NaBr$.
Sodium iodide, NaI.

Sodium Fluoride, NaF, is prepared by neutralizing hydrofluoric acid with sodium carbonate. The compound crystallizes in anhydrous cubes. It is soluble in 25 parts of cold water, and scarcely more so in hot water. It has a tendency to form double compounds with other salts, as instanced in cryolite, the double fluoride of sodium and aluminum, Al_2F_66NaF.

Sodium Chloride, NaCl. **Sodii Chloridum, U. S. P.**—Sodium chloride, or common salt, is found abundantly throughout the globe. As rock-salt it occurs in large deposits, alternating with strata of clay and gypsum, at an average depth of 100 meters. Probably the most celebrated mines are at Wieliczka, in Galicia, the deposit there being 500 miles long, 20 miles broad, and 1200 feet thick. Enormous quantities are also found in England, at Stassfurt, Germany, and in America.

Numerous salt springs also occur in many parts of the world, in which common salt is the chief constituent. These springs are especially abundant in West Virginia, Michigan, and New York, each containing a large number of these springs.

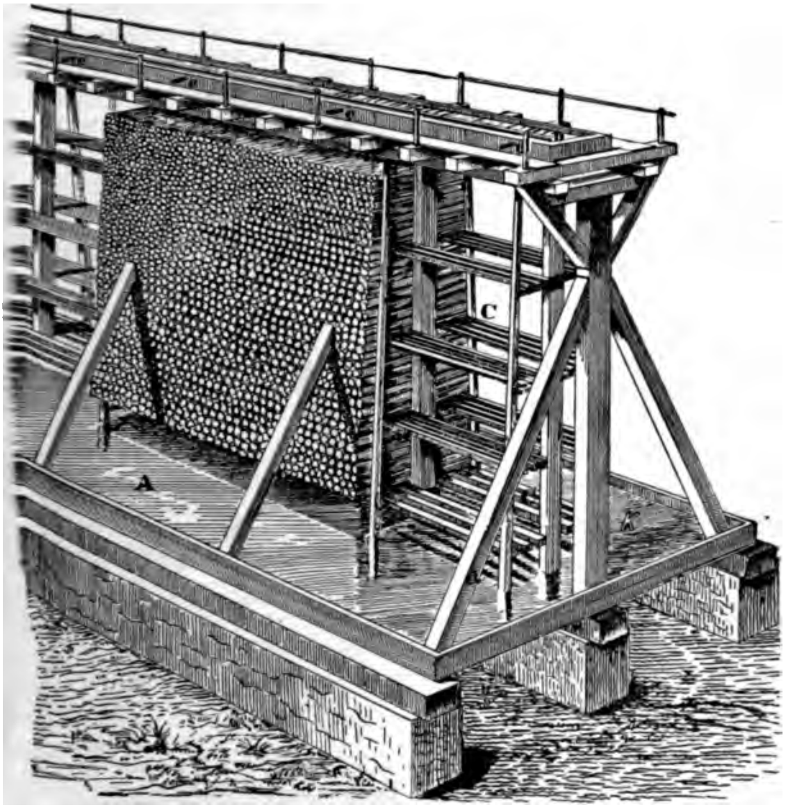
Sea water contains 3 to 4 per cent. of solid residue, three-fourths to nine-tenths of which is sodium chloride, or 2.4 to 2.8 per cent. of the sea water. There is relatively more salt in that part of the ocean situated near or crossed by the equator. Many inland seas contain a greater proportion of salt than exists in the ocean. For instance, the water of the Great Salt Lake in Utah contains over 22 per cent. of saline matter, about 90 per cent. of which is sodium chloride.

Extraction.—When sufficiently pure, rock-salt is mined and sent at once into commerce without further purification. If it is more inaccessible, or mixed with earthy matter, holes are drilled into the deposits, water is run in, and the saturated solution is either forced out by the water which enters, or it is pumped out. The salt is recovered by evaporating the solution in iron or lead boilers. Weaker salt solutions are first evaporated by the sun's rays. This is accomplished either in large shallow dikes lined with clay, as carried out with sea water in the south of France, or by allowing the solution to trickle down over a large pile of brushwood, as shown in Fig. 62. When the liquid has reached a concentration representing 15 to 20 per cent. of salt, it is run into open boilers and the evaporation completed.

The salt thus produced is quite impure and requires further treatment. In some cases it is spread on washed sand, and the more deliquescent salts liquefy and are absorbed; in other cases the crude salt is placed in baskets over the boilers in which the brine is concentrating, the steam rising dissolves the more soluble salts. Finally, crude salt may be purified by washing it with a saturated solution of pure salt.

When a purer compound is desired for chemical purposes, the purest commercial salt is carefully treated with barium chloride solution so long as a precipitate is produced, by which the sodium sulphate is decomposed, barium sulphate and sodium chloride resulting ; the barium sulphate is filtered out, and the warm filtrate is treated with a slight excess of sodium carbonate, this precipitates aluminum, barium, calcium, iron, and magnesium compounds ; after filtering clear, the solution is carefully neutralized with hydrochloric acid, and evaporated to the crystallizing point.

FIG. 62.



Evaporation of weak brines.

The output of salt in the United States in 1892 amounted to 11,585,754 barrels (280 pounds being reckoned to the barrel) ; of this Michigan supplied 3,812,054 barrels, New York 4,400,000 barrels, other States 3,373,700 barrels.

Properties.—Sodium chloride ordinarily occurs in transparent cubical crystals, or as a white, crystalline powder. It is permanent in the air, odorless, and has a pure saline taste. Water dissolves 2.8 parts at 15°, and 2.5 parts at the boiling point ; it is almost insoluble in alcohol. The solution in water has a neutral reaction. When heated the salt decrepitates ; at a red heat (about 772°) it fuses, and at a white heat it is slowly volatilized with some decomposition.

Uses.—Sodium chloride is used as a condiment, in medicine, and as a source for the preparation of other sodium salts, the most conspicuous of which are sodium sulphate and carbonate.

Sodium Bromide, NaBr. **Sodii Bromidum,** U. S. P.—The preparation of this salt is carried out similarly to the potassium salt, either by double decomposition between ferrous bromide and sodium carbonate, or by the formation of sodium bromide and bromate by the combination of bromine and sodium hydrate. The bromate is converted into bromide by fusion with charcoal.

Properties.—Sodium bromide occurs in colorless or white cubical crystals ; without odor, and with a saline, slightly bitter taste. The salt slowly attracts moisture from the air without deliquescing ; this is probably due to the fact that at ordinary temperatures it crystallizes with two molecules of water, but as found in commerce it is free from water of crystallization, the latter condition having been attained by crystallizing from a warm solution, or above 30°.

Sodium bromide is soluble in 1.2 parts of water at 15°, and in 0.5 part of boiling water ; in 13 parts of alcohol at 15°, and in 11 parts of boiling alcohol. When heated the salt melts at 712°, and at higher temperatures it is slowly volatilized with some decomposition.

Uses.—The principal use of sodium bromide is in medicine.

Sodium Iodide, NaI. **Sodii Iodidum,** U. S. P.—This salt is prepared almost exactly as the corresponding potassium salt.

Properties.—Sodium iodide occurs in colorless cubical crystals, or as a white, crystalline powder ; it is odorless, and has a saline, slightly bitter taste. It is deliquescent in moist air, and when exposed decomposes into sodium carbonate and free iodine, thereby becoming reddish-brown in color.

The salt is soluble in 0.6 part of water at 15°, and in 0.33 part of boiling water ; in 3 parts of alcohol, and in 1.4 part of boiling alcohol. When it crystallizes from water at ordinary tempera tures it contains two molecules of water of crystallization, but above 40° it separates anhydrous. When heated it melts, and at a higher temperature it volatilizes with some decomposition. Its aqueous solution is neutral to litmus paper.

Uses.—Sodium iodide has some use in medicine, as it is considered preferable to the potassium salt where its use is to be continued for some time.

SODIUM AND OXYGEN.

Sodium combines with oxygen in two proportions, resulting in the following well-defined compounds:

Sodium monoxide, Na_2O.
Sodium peroxide, Na_2O_2.

Sodium Monoxide is formed with some peroxide when sodium is burned in air. On heating to a high temperature the peroxide loses half of its oxygen, and the monoxide remains. It may also be obtained by heating together sodium hydrate and sodium:

$$NaOH + Na = Na_2O + H.$$

It is a gray mass with a conchoidal fracture. When brought in contact with water, violent action occurs with the formation of sodium hydrate.

Sodium Peroxide, Na_2O_2.—This compound is formed when sodium is heated in oxygen gas, until the weight becomes constant. It is also produced by the ignition of sodium nitrate.

Properties.—As found in commerce, sodium peroxide is a yellowish-white powder. It is very deliquescent. When thrown into water, considerable heat is evolved, and sodium hydrate and oxygen are formed, as follows:

$$Na_2O_2 + H_2O = 2NaOH + O.$$

When, however, a dilute acid is present, hydrogen dioxide results:

$$Na_2O_2 + 2HCl = 2NaCl + H_2O_2.$$

This compound has within the past few years become an article of commerce for bleaching and oxidizing purposes.

It contains about 20 per cent. of available oxygen.

Sodium Hydrate, **Soda,** U. S. P. (Sodium Hydroxide, Caustic Soda), NaOH.—The simplest method or forming the hydrate of sodium is by throwing the metal on water:

$$Na_2 + 2H_2O = 2NaOH + H_2.$$

This method requires considerable care, as the fused metal is liable to be thrown about. It is employed when a very pure product is desired.

A cheaper and more usual method consists in dissolving 3 parts of sodium carbonate crystals in 15 parts of water, heating to the boiling point, and adding in small portions at a time milk of lime, obtained by slaking 1 part of quick-lime, calcium oxide, with 3 parts of water; this mixture is boiled for some time, water is added to replace that which is evaporated, until a portion of the clear liquid fails to give effervescence on the addition of dilute acid:

$$\underset{\substack{\text{Sodium}\\\text{Carbonate.}}}{Na_2CO_3} + \underset{\substack{\text{Calcium}\\\text{Hydrate.}}}{Ca(OH)_2} = \underset{\substack{\text{Sodium}\\\text{Hydrate.}}}{2NaOH} + \underset{\substack{\text{Calcium}\\\text{Carbonate.}}}{CaCO_3}.$$

The clear liquid is decanted from the precipitate and evaporated in an iron dish to a specific gravity of 1.170, when the concentration is completed in a silver dish and the fused product poured into silver moulds, similar to those used for potassium hydrate. (See Fig. 60.) On the commercial scale sodium hydrate is produced by a modification of the Leblanc process for preparing sodium carbonate by the addition of more coal in the black-ash fusion; the reaction being as follows:

$$CaCO_3 + C = CaO + 2CO.$$
$$Na_2CO_3 + CaO + H_2O = 2NaOH + CaCO_3.$$

Sodium hydrate is also obtained as one of the products in the electrolysis of common salt on a large scale.

That which is prepared in large quantities comes in commerce in iron drums; 54,331,533 pounds were imported in 1892.

Properties.—The sodium hydrate which is used for pharmaceutical and medicinal purposes occurs in dry, white, translucen pencils, showing a crystalline structure, free from odor, and having an acrid and caustic taste. When exposed to moist air i rapidly deliquesces; in dry air it first becomes coated with a dr film of carbonate. It is soluble in 1.7 parts of water at 15°, an in 0.8 part of boiling water; very soluble in alcohol.

On the application of heat sodium hydrate melts at 525° to clear oily liquid, and at a bright red heat it is slowly volatilize unchanged. The solution, even when very dilute, gives strongly alkaline reaction with litmus paper.

When sodium hydrate is free from water it has a specific gravit of 2.13. The very concentrated aqueous solution, when coole to 0°, deposits crystals of the formula $NaOH.3\frac{1}{2}H_2O$. Water always present in the commercial article; that coming in sticks contains at least 10 per cent. of moisture. Alcohol is used to free the commercial compound from impurities, since the latter are of a character to be insoluble in this solvent. The commercial preparation, which has been purified by this means, is known as "soda by alcohol."

Liquor Sodæ, U. S. P., is made from sodium carbonate and lime according to one of the preceding processes, or else by dissolving 56 grammes of sodium hydrate (containing 90 per cent. of absolute NaOH) in sufficient water to make 1 liter. The resulting solution has a specific gravity of 1.059 at 15°, and contains about 5 per cent. of NaOH.

Uses.—Sodium hydrate is used externally as a caustic, and it is extensively employed as a chemical reagent. The most important technical use of the commercial product is in the preparation of soap.

OXYGEN SALTS OF SODIUM AND HALOGENS.

Sodium Hypochlorite, NaOCl.—This compound only occurs in solution. Officially it is known as **Liquor Sodæ Chloratæ**, or Labarraque's Solution. This solution is made by mixing solutions of sodium carbonate and chlorinated lime; the reaction is as follows:

$$\underbrace{Ca(ClO)_2 + CaCl_2}_{\text{Chlorinated Lime.}} + \underbrace{2Na_2CO_3}_{\text{Sodium Carbonate.}} = \underbrace{2NaClO + 2NaCl}_{\text{Labarraque's Solution.}} + \underbrace{2CaCO_3}_{\text{Calcium Carbonate.}}$$

The clear supernatant liquid, after decantation, should contain 2.6 per cent. of available chlorine. This solution has a specific gravity of about 1.059 at 15°, and contains, in addition to the hypochlorite, sodium chloride and carbonate.

Sodium Chlorate, $NaClO_3$. **Sodii Chloras**, U. S. P.—Sodium chlorate may be prepared in the same manner as the corresponding potassium salt. On account of its greater solubility, however, its separation by crystallization is not so readily accomplished. It has been recommended, therefore, to prepare it for medicinal use by double decomposition between sodium bitartrate and potassium chlorate, the following reaction occurring:

$$NaHC_4H_4O_6 + KClO_3 = NaClO_3 + KHC_4H_4O_6.$$

For this purpose a concentrated solution of 19.5 parts of tartaric acid are added to 18.3 parts of crystallized sodium carbonate, previously dissolved in an equal quantity of hot water. The resulting solution, while hot, is mixed with a hot solution of 16 parts of potassium chlorate in 50 to 60 parts of water. The whole is allowed to stand 24 hours for the potassium bitartrate to crystallize out. After filtering from the latter, the filtrate is evaporated carefully to dryness, dissolved in the smallest possible amount of water, filtered, and allowed to crystallize. As thus prepared, a pure product may, no doubt, be obtained, but, as a matter of fact, it is liable to be contaminated with tartaric acid. A process which yields a purer product consists in adding a hot solution of 9 parts of potassium chlorate to a similar solution of 7 parts of sodium silico-fluoride, and boiling:

$$2KClO_3 + Na_2SiF_6 = 2NaClO_3 + K_2SiF_6.$$

The subsequent treatment is the same as in the preceding process. The product in this case has the advantage of being free from the possible contamination with organic matter.

Sodium chlorate occurs in colorless, transparent crystals, or as a white, crystalline powder. Its taste is more decidedly saline and cooling than the corresponding potassium salt. It is soluble in 1.1 parts of water at 15°, and in 0.5 part of boiling water, in 100 parts of alcohol, and in 40 parts of boiling alcohol; it is also soluble in 5 parts of glycerin. When heated, the salt melts and gives off oxygen, leaving a residue of sodium chloride.

On account of its greater solubility the salt has been used considerably in place of the potassium chlorate in calico printing and in the manufacture of aniline black.

Sodium Bromate, $NaBrO_3$, may, like the potassium bromate, be prepared during the manufacture of the corresponding bromide. It is soluble in about 3 parts of water at 15°. In other respects it resembles the potassium salt.

Sodium Iodate, $NaIO_3$, is prepared similarly to the preceding salt, and crystallizes with a variable proportion of water. It is soluble in some 14 parts of water.

SODIUM AND SULPHUR AND THEIR OXYGEN SALTS.

These compounds closely resemble the mono-, di-, tri-, and polysulphides of potassium, and may be prepared in a similar manner.

Sodium Hyposulphite, $NaHSO_2$.—This must not be confounded with the thiosulphate, $Na_2S_2O_3.5H_2O$, which is commercially known as hyposulphite.

The true sodium hyposulphite is prepared by reducing a concentrated solution of acid sodium sulphite in a well-corked bottle with metallic zinc. The mixture is kept cool for about a half-hour, when a white precipitate of sodium zinc sulphite separates. The clear supernatant solution is then poured off into three times its volume of strong alcohol, and the resulting liquid poured into a bottle, completely filling it. The bottle is then tightly corked to exclude air, and set aside. A second crop of the sodium zinc sulphite crystals again forms, and the clear liquid is poured from these into a bottle, and excluded from the air as before. After some hours' standing, crystals of the sodium hyposulphite are seen to separate. They are filtered out, quickly pressed between folds of filtering paper, and dried in a vacuum. The resulting salt may be purified by solution in water and reprecipitation by alcohol as before.

This compound is used in dyeing, to reduce indigo, and as a laboratory reagent, where the estimation of free oxygen is involved.

Sodium Sulphite, $Na_2SO_3.7H_2O$. **Sodii Sulphis**, U. S. P.—Normal sodium sulphite is prepared by saturating a solution of sodium carbonate with sulphur dioxide, and then adding an amount of sodium carbonate, previously dissolved in water, equal to that first employed:

$$\underset{\substack{\text{Sodium}\\\text{Carbonate.}}}{Na_2CO_3} + \underset{\substack{\text{Sulphur}\\\text{Dioxide.}}}{2SO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Acid Sodium}\\\text{Sulphite.}}}{2NaHSO_3} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{CO_2}.$$

$$\underset{\substack{\text{Acid Sodium}\\\text{Sulphite.}}}{2NaHSO_3} + \underset{\substack{\text{Sodium}\\\text{Carbonate.}}}{Na_2CO_3} = \underset{\substack{\text{Sodium}\\\text{Sulphite.}}}{2Na_2SO_3} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O}.$$

The solution is then carefully evaporated to crystallization.

If the solution be heated to the boiling point, the anhydrous sodium sulphite separates, and redissolves on cooling.

Properties.—The official salt occurs in colorless, monoclinic prisms; it is without odor, and has a cooling, saline, somewhat sulphurous taste; it effloresces when exposed to air, and is slowly oxidized to sulphate.

It is soluble in 4 parts of water at 15°, and in 0.9 part of boiling water; it is scarcely soluble in alcohol. When the salt is gently heated, it softens somewhat, without fusing, and above 100° it loses its water of crystallization, amounting to 50 per cent., without the crystals changing their shape. At a red heat, the salt fuses to reddish-yellow masses of sodium sulphate and sulphide.

The aqueous solution is either neutral or faintly alkaline to litmus paper.

Acid Sodium Sulphite, $NaHSO_3$, **Sodii Bisulphis**, U. S. P., is prepared, as stated under the preceding salt, when a solution of sodium carbonate is saturated with sulphur dioxide; the salt separates out in turbid crystals on cooling the solution.

Commercially it is much used in solution, from which, however, it may be crystallized, or precipitated by alcohol.

Properties.—The salt slowly evolves sulphur dioxide, and has a disagreeable, sulphurous taste. It is soluble at 15° in [illegible] parts of water and in 72 parts of alcohol, and in about 2 parts of boiling water and in 49 parts of boiling alcohol. When strongly heated, the vapors of sulphur and sulphur dioxide are evolved, and a residue of sodium sulphate remains. The aqueous solution imparts an acid reaction to litmus paper.

The official requirements demand a salt of 90 per cent. purity, but it is not often found in commerce of this strength.

Uses.—The salt and its solution are used largely as a preservative, and as a bleaching agent. Sulphur dioxide is readily and abundantly evolved on the addition of an acid.

Sodium Sulphate, $Na_2SO_4.10H_2O$. **Sodii Sulphas**, U. S. P. The anhydrous salt is known as *salt-cake*, while the official compound with 10 molecules of water is known as *Glauber's salt*, after Glauber, who, in 1658, first described it under the name of *sal mirabile*. Sodium sulphate is widely diffused in nature. In the anhydrous condition it is found as the mineral thenardite, and in the hydrous form as mirabilite; the former is found in Spain and on Vesuvius, and the latter throughout the globe; it exists in sea water and in many mineral springs, chief of which is that at Carlsbad. Large amounts occur in a nearly pure state, in solution, in many lakes throughout the arid regions of western United States. A number of these lakes exist near Laramie, Wyoming, where the salt occurs in various degrees of purity, amounting in some cases to over 99 per cent. The depth of this deposit is 20 to 30 feet.

Preparation.—In addition to being found native, sodium sulphate is a by-product in many chemical processes, and is also produced in enormous quantities as a preliminary step in the Leblanc process for manufacturing sodium carbonate. Large quantities are produced from the natural product in Wyoming; this natural product is dehydrated before sending into commerce. The official salt occurs in transparent monoclinic prisms or granular crystals, the commercial salt is frequently covered with efflorescence; it is without odor, and has a bitter, saline taste.

Sodium sulphate is soluble in 2.8 parts of water at 15°, and in 0.47 part of boiling water; at 34° water exerts the maximum solvent action, 1 part of the salt requiring 0.25 part of water; if this solution be heated, rhombic crystals of the anhydrous salt separate out.

Sodium sulphate fuses when heated to 33°, and at 100° it loses all its water, amounting to 55.9 per cent. At a red heat the anhydrous salt fuses without decomposition.

Uses.—Sodium sulphate has some use in medicine, but its greatest consumption is in the manufacture of sodium carbonate; it is also extensively employed in glass manufacture.

Acid Sodium Sulphate, $NaHSO_4$, is known as bisulphate of soda. It is prepared by heating 16 parts of sodium sulphate with 10 parts of pure concentrated sulphuric acid until they liquefy, and then dissolving the cooled, white, crystalline mass in twice its weight of water; by evaporating at 50° the anhydrous salt is obtained in triclinic prisms. When the crystallization takes place at the ordinary temperature, monoclinic prisms, with one molecule of water, $NaHSO_4.H_2O$, are formed.

There are other sodium sulphates of minor importance, which are very similar to the corresponding potassium salts, to which the reader is referred.

Sodium Thiosulphate, $Na_2S_2O_3.5H_2O$. **Sodii Hyposulphis, U. S. P.**—This salt is commercially, but incorrectly, known as hyposulphite of soda. It was discovered in 1799 by Chaussier.

Preparation.—Sodium thiosulphate is prepared by boiling a solution of sodium sulphite with sulphur:

$$Na_2SO_3 + S = Na_2S_2O_3.$$

The commercial source is from the *black ash* residue, after extraction of sodium carbonate in the alkali manufacture. When this residue is exposed to air for some time, the calcium sulphide, or oxysulphide, therein contained, is oxidized to thiosulphate, as follows:

$$\underset{\text{Calcium Sulphide.}}{2CaS} + \underset{\text{Oxygen.}}{2O_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Calcium Thiosulphate.,}}{CaS_2O_3} + \underset{\text{Calcium Hydrate.}}{Ca(OH)_2}.$$

The thiosulphate is extracted from the mass with water, and the resulting solution decomposed with sodium sulphate as follows:

$$\underset{\text{Calcium Thiosulphate.}}{CaS_2O_3} + \underset{\text{Sodium Sulphate.}}{Na_2SO_4} = \underset{\text{Sodium Thiosulphate.}}{Na_2S_2O_3} + \underset{\text{Calcium Sulphate.}}{CaSO_4}.$$

Properties.—Sodium thiosulphate forms large, colorless, well-defined monoclinic crystals; odorless, with a saline, cooling, afterwards bitter taste. It gives a neutral reaction, and is permanent in dry air. Above 33° it effloresces, and at 50° melts in its water of crystallization. At 100° it loses all its water, amounting to 36.3 per cent., and at a red heat it is decomposed, evolving sulphur which escapes, leaving a residue of sodium sulphate and sulphide.

Sodium thiosulphate is soluble in 0.65 part of water at 15°; at the boiling temperature its solution is rapidly decomposed. It is insoluble in alcohol.

The chloride, bromide, and iodide of silver are readily soluble in solutions of sodium thiosulphate, forming a double salt as follows:

$$AgCl + Na_2S_2O_3 = NaAgS_2O_3 + NaCl.$$

Iodine is also dissolved by an aqueous solution of sodium thiosulphate, sodium iodide and tetrathionate being formed:

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

Chlorine acts in a similar manner, which fact has given to the salt the name of *antichlor;* on this account it has extensive use in removing the excess of chlorine in bleaching operations. It is also used in photography, because of the property it possesses of dissolving the halogen compounds of silver.

OXYGEN SALTS OF SODIUM AND NITROGEN.

Sodium Nitrate, $NaNO_3$. **Sodii Nitras,** U. S. P.—In 1683 Bohn discovered this salt, which was more thoroughly investigated by Duhamel in 1736, and Marggraf in 1761. In 1820 it was first shipped from South America to European ports.

Occurrence.—Sodium nitrate is found as a natural deposit in parts of South America, chiefly in Chili, Peru, Bolivia, and the province of Bahia in Brazil. The Atacama Desert extends through the northern part of Chili into the southern part of Peru. It is in Atacama, Chili, Tarapaca, Peru, and the interlying region that the most extensive deposits occur. The district covers hundreds of miles, is practically rainless, and is especially favorable for the recovery of a salt like this, which is soluble in water. The crude deposit is termed "caliche," and one tract alone extends 40 miles in length, and 1 to 2 miles in width.

A characteristic nitrate *pampa*, or *calichero*, as it is called, consists of about the following strata: First, a layer of sand and gravel, about 1 to 2 inches deep; then a 6-inch layer of a white, friable substance consisting largely of calcium sulphate; below this is a stratum from 2 to 10 feet in thickness, consisting of earth and stones; then there is a layer 1 to 3 feet thick of a substance known as *costra*, which is low-grade *caliche*, composed of chlorides, feldspar, and earthy matter. The *caliche*, or crude sodium nitrate, lies below this; it forms a layer from 1½ to 2 feet in thickness. In the Tarapaca district this layer is much thicker, ranging from 4 to 12 feet. Below the sodium nitrate deposit is a stratum of fine clay 3 feet in depth, and resting on porphyritic rocks.

The value of the *caliche* varies from 15 to 65 per cent. sodium nitrate. The different grades are mixed so as to make an average product containing about 35 per cent.

Extraction.—The crude *caliche* is boiled with water until the liquor registers 110° Tw. at 120°, and the clear solution run into crystallizing tanks. The residue is boiled with water a second time, which usually completes the exhaustion. The liquor in the crystallizing tanks deposits its crystals of the nitrate in from 4 to 6 days, according to the temperature.

The mother liquor is then run off to the iodine house, where that valuable element is removed. The crystals of sodium nitrate are thrown out on draining-boards, washed once with a little cold water, allowed to dry, and are then packed in bags for shipment. As water is scarce in this dry region, all washings are saved and all steam is condensed as far as possible. In some places water is brought as far as 80 miles. The commercial sodium nitrate, prepared as above described, consists of 96 per cent. nitrate, with small quantities of chlorides, sulphates, moisture, and insoluble matter.

Properties.—For medicinal use the commercial salt would require purification by recrystallization. It is officially described as occurring in "colorless, transparent, rhombohedral crystals, odorless, and having a cooling, saline, and slightly bitter taste. Deliquescent in moist air. Soluble, at 15°, in 1.3 parts of water, and in about 100 parts of alcohol; in 0.6 part of boiling water, and in 40 parts of boiling alcohol."

When 75 parts of sodium nitrate are dissolved in 100 parts of water at 13.2°, the temperature falls to —5.2°.

On the application of heat, sodium nitrate melts at 312°, without decomposition; at a higher temperature it evolves oxygen and is converted into nitrite. The aqueous solution of the salt has a neutral reaction towards litmus paper.

Uses.—Sodium nitrate is used extensively as a fertilizer, as a preservative agent for meat, and for the preparation of potassium nitrate by double decomposition with potassium chloride. Since it is cheaper than the potassium salt, it is used in the preparation of nitric acid. It cannot replace the potassium salt in the manufacture of gunpowder, because of its tendency to absorb moisture. The world's consumption of sodium nitrate amounted to 845,000 tons in 1893, of which about 100,000 tons came to the United States.

Sodium Nitrite, $NaNO_2$, **Sodii Nitris,** U. S. P., is prepared by heating 100 parts of sodium nitrate with 285 parts metallic lead, in an iron vessel, to 500°:

$$NaNO_3 + Pb = NaNO_2 + PbO.$$

The fused mass is treated with water, filtered, and carbon dioxide passed through the filtrate in order to remove the last traces of lead. Finally, the salt is purified by repeated crystallization.

Properties.—As usually found in commerce, sodium nitrite is in opaque, fused masses or sticks. These have a yellowish-white color, and are made up of microscopic, prismatic crystals. The salt is odorless, has a mild, saline taste, and when exposed to the air deliquesces and is gradually oxidized to nitrate.

Sodium nitrite is soluble in about 1.5 parts of water at 15°; very soluble in boiling water, and only slightly soluble in alcohol. On the application of heat, the salt melts, and at a red heat it decomposes, with the formation of oxygen, nitrogen, nitrogen dioxide, and sodium oxide. The aqueous solution reacts alkaline towards litmus paper.

This salt was made official because of its use in the manufacture of spirit of nitrous ether. The Pharmacopœia requires that it shall contain not less than 97.6 per cent. of the pure salt.

Sodium nitrite has considerable use as a chemical reagent, being usually employed when a soluble nitrite is demanded; it is also employed by the color manufacturers.

OXYGEN SALTS OF SODIUM AND PHOSPHORUS.

Sodium Orthophosphates.—There are three compounds of sodium with orthophosphoric acid, as follows:

Trisodium orthophosphate, $Na_3PO_4.12H_2O$.
Disodium orthophosphate, $Na_2HPO_4.12H_2O$.
Monosodium orthophosphate, $NaH_2PO_4.H_2O$.

The first one of these, which is also known as the neutral sodium phosphate, is obtained when a slight excess of sodium hydrate is added to the disodium salt or to orthophosphoric acid, and the solution evaporated. It separates in six-sided prisms, is easily soluble in water, and the resulting solution reacts alkaline towards litmus. When exposed to the air the solution absorbs carbon dioxide, sodium carbonate and the disodium salt resulting.

Disodium Orthophosphate, $Na_2HPO_4.12H_2O$.—This salt is official under the name of **Sodii Phosphas,** U. S. P., but is generally known in commerce as "phosphate of soda." It is widely distributed in the animal economy, especially in the urine, where it is found to the extent of from .3 to .5 per cent.

Sodium phosphate is formed when sodium carbonate is added to phosphoric acid until a faintly alkaline reaction is obtained. Below 33° crystallization takes place.

Properties.—These crystals contain 12 molecules of water, and rapidly effloresce on exposure to the air, losing 5 molecules of water (25.1 per cent.). They occur in large, colorless, monoclinic prisms, odorless, and having a cooling, saline taste. The salt is soluble in 5.8 parts of water at 15° and in 1.5 parts of boiling water; it is insoluble in alcohol.

On the application of heat, sodium phosphate fuses at 40°; at 100° it loses all its water of crystallization, amounting to 60.3 per cent., and at a red heat it is converted into sodium pyrophosphate. The aqueous solution reacts slightly alkaline towards litmus paper, but does not affect phenolphtalein.

Uses.—Sodium phosphate is used somewhat in medicine, largely as a reagent, and to a certain extent in the dyeing industry.

Monosodium Orthophosphate, $NaH_2PO_4.H_2O$.—When ordinary sodium phosphate and orthophosphoric acid are mixed and evaporated, the monosodium salt separates with one molecule of water of crystallization. These crystals occur in rhombic prisms, and their aqueous solution has an acid reaction.

Sodium Pyrophosphate, $Na_4P_2O_7.10H_2O$. **Sodii Pyrophosphas,** U. S. P.—The simplest method of obtaining this salt is by heating the ordinary sodium phosphate to 250°, or more rapidly by increasing the temperature to low redness, until a sample taken out and dissolved in water gives no yellowish color to the precipitate with silver nitrate. The following expresses the reaction:

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

This operation may be conducted in an iron vessel, but one of silver is preferable. After the conversion is complete, the cooled mass is dissolved in 5 parts of hot water, filtered, and the filtered solution allowed to crystallize.

Sodium pyrophosphate occurs in "colorless, transparent, monoclinic prisms, or a crystalline powder, odorless, and having a cooling, saline, and feebly alkaline taste." The crystals are permanent under most circumstances, but effloresce slightly in dry air.

The salt is soluble in 12 parts of water at 15°, and in 1.1 parts of boiling water; alcohol does not dissolve it. The aqueous solution is slightly alkaline to litmus and phenolphtalein. When heated to 100°, the salt loses its water of crystallization, amounting to 40.34 per cent. Above this temperature it fuses to a clear liquid, which solidifies in a crystalline mass.

Disodium Pyrophosphate, $Na_2H_2P_2O_7.6H_2O$, is prepared by heating the official sodium phosphate to 150° with strong hydrochloric acid, or by dissolving the normal pyrophosphate in acetic acid and precipitating by alcohol. As thus obtained, it occurs as a white, crystalline powder. Its aqueous solution has an acid reaction.

Sodium Metaphosphate, $NaPO_3$, is formed by heating the ordinary phosphate to bright redness for some minutes. This compound is scarcely soluble in water; it exists in several polymeric modifications, corresponding to the various polymeric metaphosphoric acids; these modified salts are more soluble in water.

Sodium Hypophosphite, $NaPH_2O_2.H_2O$. **Sodii Hypophosphis,** U. S. P.—Sodium hypophosphite is obtained by adding solution of sodium carbonate to one of calcium hypophosphite as long as a precipitate is produced. The filtered solution is evaporated at a low temperature, and concentration is completed in a vacuum. Dangerous explosions have resulted from too rapid evaporation of this solution, even a water-bath temperature may result disastrously.

Properties.—This salt occurs in pearly, tabular crystals, or in a white, granular powder; it is without odor, but possesses a bitterish-sweet, saline taste. It is very deliquescent on exposure to moist air, and the solution is neutral to litmus paper.

Sodium hypophosphite is soluble in 1 part of water and in 30 parts of alcohol at 15°; it is dissolved by 0.12 part of boiling water and by 1 part of boiling alcohol; in absolute alcohol it is slightly soluble, but insoluble in ether.

On carefully heating a small quantity of the salt in a test-tube, it first loses water of crystallization, and at 200° it is decomposed with the evolution of spontaneously inflammable hydrogen phosphide and some hydrogen, which burn with a yellow flame.

Sodium hypophosphite should not be triturated with nitrates, chlorates, permanganates, or other oxidizing agents, as violent explosions thereby result.

OXYGEN SALTS OF SODIUM AND BORON.

Sodium Borate, $Na_2B_4O_7.10H_2O$. **Sodii Boras**, U. S. P.

History.—Borax was known to the ancients and to the alchemists. Its true chemical character was not understood until 1747, when Baron pointed out the fact that it consisted of boric acid (then called sedative salt) and soda.

Occurrence.—Originally borax was known in certain lakes of Thibet, later it was brought from India and Persia, and was found in smaller quantities in various parts of the world. Rich deposits are found in the nitre regions of Chili and Peru, and in Ecuador. The abundant deposits of borax in the United States were not discovered until 1856, and not worked until 1864. The discovery appears to have been made by Dr. Veatch, at Clear Lake, California. Since that time numerous other deposits have been discovered in California and Nevada. In some of these localities the base is calcium instead of sodium ; in South America, for instance, the mineral *boronatrocalcite*, $Na_2B_4O_7.2CaB_4O_7.18H_2O$, is chiefly found, while the *borocalcite*, $CaB_4O_7.4H_2O$, is found in these as well as in many other places. One bed of this latter mineral, near Death Valley, in California, has an average depth of six feet. It is locally known as *colemanite*, from Coleman, the discoverer. This mineral is also known as *ulexite*, and, from the nature of the crystallizations, it is termed cotton-balls by the inhabitants.

Extraction.—Crude borax is known as *tincal.* This crude product in many cases only requires to be dissolved in water and allowed to crystallize in order to make it sufficiently pure to be sent into commerce. In other deposits there is much matter of a greasy nature, which must first be removed by washing with a weak solution of sodium or calcium hydrate. The deposits in this country, however, are of such purity as merely to require recrystallization. When *borocalcite* or *ulexite* is used, it is boiled with water and sodium carbonate, the result being sodium borate and calcium carbonate. Much of the borax formerly consumed in the Eastern Hemisphere was made by neutralizing the native boric acid of Tuscany with sodium carbonate. The output of borax in the United States is not far from 10,000,000 pounds annually, and instead of importing it at a high price, as was the case previous to 1864, it is now exported in large quantities.

Properties.—Sodium borate occurs in colorless, transparent, prismatic crystals, or as a white powder; it is odorless, and has a sweetish, alkaline taste. In warm, dry air it is slightly efflorescent.

The salt dissolves in 16 parts of water at 15°, and 0.5 part of boiling water; it is insoluble in alcohol. At 80° it is soluble in 1 part of glycerin. On the application of heat, borax first loses a part of its water of crystallization, and, without melting, swells to a white, porous mass. When the heat is increased to redness, the remainder of the water is driven off, amounting to 47.14 per cent., and the salt fuses to a colorless liquid, which on cooling hardens to a transparent glass known as borax glass. The aqueous solution of the salt reacts alkaline towards litmus paper, and colors yellow turmeric paper brown.

Uses.—On account of its solvent action on metallic oxides, borax is largely used in soldering and welding. Its extended use in metallurgical operations and in blowpipe analysis is well known. It enters into the composition of some soaps, is used as a preservative, and is employed in the manufacture of certain kinds of glass, and in some enamels.

Octohedral Borax is a variety with 5 molecules of water of crystallization. It is formed by allowing crystallization to take place above 60°. This is accomplished by dissolving ordinary borax in boiling water until the solution has a specific gravity of 1.246, and then allowing it to cool slowly; the crystallization begins when the temperature reaches 79°. Below 56° ordinary prismatic borax crystallizes.

Sodium Metaborate, $NaBO_2.4H_2O$.—This salt is formed when 1 molecule of borax is fused with 1 molecule of sodium carbonate, the product is the anhydrous salt, which, when dissolved in water and allowed to crystallize, separates with 4 molecules of water.

Sodium Orthoborate, Na_3BO_3.—When boron trioxide is fused with sodium hydrate the following reaction takes place:

$$\underset{\text{Boron Trioxide.}}{B_2O_3} + \underset{\text{Sodium Hydrate.}}{6NaOH} = \underset{\text{Sodium Orthoborate.}}{2Na_3BO_3} + \underset{\text{Water.}}{3H_2O}.$$

This salt is very unstable, and cannot exist in solution, since it is converted by water into the metaborate.

OXYGEN SALTS OF SODIUM AND SILICON.

SODIUM SILICATES.

Sodium silicate is a constituent of many minerals and of glass. There are at least three compounds of silicic acid with sodium, which are formed according to the proportion of the constituents entering into the reaction. When quantities of silica and sodium carbonate, equal to their respective molecular weights, are fused together, sodium metasilicate, Na_2SiO_3, is formed.

This compound is soluble in water, and when it is dissolved in that liquid and slowly evaporated, it separates in monoclinic crystals with 6 molecules of water of crystallization. If in the fusion an excess of sodium carbonate be used, the trisilicate, $Na_8Si_3O_{10}$, is formed.

Commercial sodium silicate, or *water glass*, consists chiefly of sodium tetrasilicate, $Na_2S_4O_9$. It is prepared by fusing together 45 parts of powdered quartz or fine sand, 23 parts of dry sodium carbonate, and 3 parts of charcoal. The fused product is run into a tank of water, which has the effect of converting it into small porous masses, which are more easily dissolved in water. The solution in water is a thick, viscid liquid, which forms the **Liquor Sodii Silicatis, U. S. P.** It is officially described as follows: "A semi-transparent, almost colorless, or yellowish, or pale greenish-yellow, viscid liquid, odorless, having a sharp, saline, and alkaline taste, and an alkaline reaction. Specific gravity, 1.300 to 1.400 at 15°."

Soluble glass is used largely as a bandaging material, enters into the composition of many cements, and is used in large quantities in the manufacture of silicated soaps.

Sodium Fluosilicate, Na_2SiF_6.—This compound is also known as sodium silicofluoride. It is prepared by neutralizing hydrofluosilicic acid with sodium hydrate or carbonate. Like the corresponding potassium salt, it is not very soluble in cold water. It is stated to have powerful antiseptic properties, and has been introduced into medicine under the name of "Salufer."

OXYGEN SALTS OF SODIUM AND CARBON.

Sodium Carbonate, $Na_2CO_3.10H_2O$. **Sodii Carbonas, U.S.P.**

History.—Sodium carbonate, or soda, has been known since the earliest times. It was not originally distinguished from potash, both being designated by the term *nitrum*.

Duhamel, in 1736, and Marggraf, in 1759, were the first to draw a sharp distinction between the two; the former showed the base of common salt, borax, and the ashes of sea plants to be one and the same; the latter designated soda as *mineral alkali*, and distinguished it from potash by the yellow color it imparted to the flame.

Nearly all the soda was obtained previous to 1793 from the ashes of sea plants, called ***varec*** or ***kelp***. These sea-weeds were collected on the northwest coasts of France, Ireland, and Scotland.

One of the immediate results of the French Revolution was to cause a demand for soda from some other source than sea-weeds. On investigating the various processes, it was found that an apothecary, Nicolas Leblanc, associated with Dizé, was operating a small manufactory at St. Denis, in which he used sea salt to furnish the sodium for his sodium carbonate. The manufactory became a national establishment, and was successfully at work in 1794. Other manufactories by this process were more successful at Marseilles, and the original one was soon closed. The industry was established in England in 1823 by Muspratt.

There is probably no operation in the whole field of industrial chemistry that has undergone so few fundamental changes. So far as the material employed and the reactions involved are concerned, they remain the same as in the original process. It is true that many improvements have been introduced, but they have been of a mechanical nature or have related to the utilization of waste material. In more recent times entirely different processes have been established, the most successful ones being that by Thomsen (1851), in which *cryolite* is used, and that by Solvay (1873), known as the *ammonia-soda* process.

Occurrence.—Sodium carbonate is found in the ash of all plants, but especially in that from sea plants and those growing near salt waters. It is also found in the waters of many mineral springs, often in the form of bicarbonate. An efflorescence or deposit, consisting largely of sodium carbonate, occurs in the soil in many rainless localities, as in Egypt, Mexico, parts of South America, and in the drier parts of the United States, there being unknown quantities in California, Wyoming, and Nevada, and probably in some other Western States. The native product in this country was produced to the amount of 2500 tons in 1893, valued at 12,500 dollars. That from the soda lakes of Egy is still shipped from Alexandria.

Preparation.—1. *Native Soda.*—The soda which occurs nature consists almost entirely of the sesquicarbonate, having formula $2NaHCO_3.Na_2CO_3.2H_2O$. That which is brought fr Egypt is usually known as *Trona-soda*, that from South Ame (Colombia) and Mexico is called *Urao-soda*, and the small q tity brought into commerce from Hungary is known as *Szek*

2. *Soda from the Ashes of Plants.*—The amount found in the ashes of sea and sea-coast plants is from 5 to 30 per cent. The soda from Spain is usually known as *Salsola soda* and *Barilla;* that from the south of France is called *Salicox* or *Blanquette* soda; and that prepared from the species of Fucus, used also in the preparation of bromine and iodine, is called *Kelp* soda in Scotland, and *Varec* soda in Normandy and the Channel Islands. Potassium is far more widely distributed in plants than sodium, but those plants growing in or near the salt water take up large quantities of sodium chloride and convert it into salts of the organic acids.

3. *The Leblanc Process.*—When sodium carbonate is manufactured by this method, the first step consists in converting sodium chloride into sulphate; this part of the operation is known as the salt-cake process. It consists in decomposing the sodium chloride in a furnace, as shown in Fig. 44, page 140, with chamber acid (sulphuric acid having a specific gravity of 1.60 to 1.70). In many works a double furnace is used, as shown in Fig. 63. The charge of salt, usually amounting to several hundred pounds, is placed in the central pan, and an equal quantity of the sulphuric acid is run in; there is an immediate evolution of large quantities of hydrochloric acid, according to the following reaction:

$$\underset{\text{Sodium Chloride.}}{\mathrm{NaCl}} + \underset{\text{Sulphuric Acid.}}{\mathrm{H_2SO_4}} = \underset{\text{Acid Sodium Sulphate.}}{\mathrm{NaHSO_4}} + \underset{\text{Hydrochloric Acid.}}{\mathrm{HCl}}.$$

The central pan in which this reaction takes place is of iron, and is heated by a fire underneath. The hydrochloric acid is passed into coke towers (see Fig. 45, page 141) to be condensed and dissolved by cold water, forming the commercial hydrochloric or muriatic acid. The residue in the pan consists of acid sodium sulphate with some undecomposed chloride. At the expiration of about an hour the mass is raked into one of the hearths or roasters on either side; here the reaction is completed by the higher heat from the furnaces at each end:

$$\underset{\text{Acid Sodium Sulphate.}}{\mathrm{NaHSO_4}} + \underset{\text{Sodium Chloride.}}{\mathrm{NaCl}} = \underset{\text{Sodium Sulphate.}}{\mathrm{Na_2SO_4}} + \underset{\text{Hydrochloric Acid.}}{\mathrm{HCl}}.$$

The hydrochloric acid which is evolved, is recovered as in the preceding part of the operation. The salt which remains consists of about 95 per cent. sodium sulphate, with small quantities of the acid sulphate, sodium chloride, calcium sulphate, ferric oxide, and insoluble matter; it is commercially known as *salt-cake*, or frequently simply as *sulphate*.

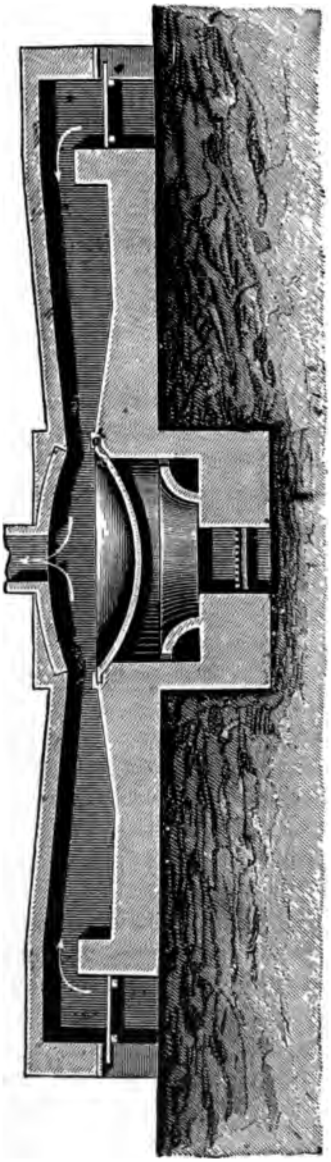


FIG. 63.

Salt-cake furnace.

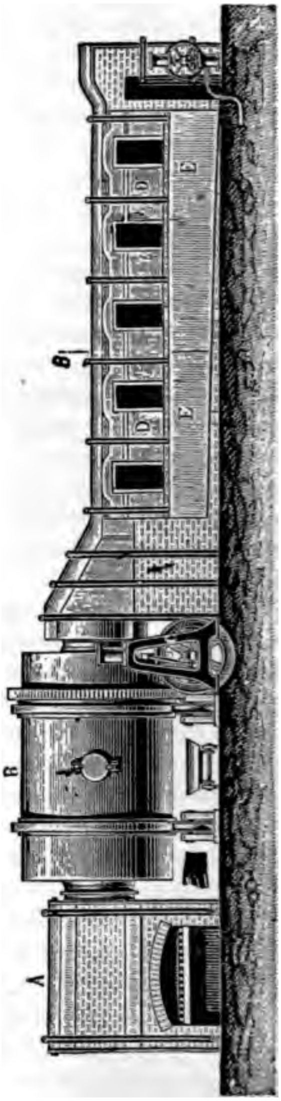


FIG. 64.

Revolving black-ash furnace.

The sulphate is converted into carbonate by the *black-ash process*. This operation consists in fusing an intimate mixture of salt-cake, calcium carbonate or limestone, and coal. The reaction takes place by two steps, as follows :

$$\begin{array}{ccccccc} Na_2SO_4 & + & 4C & = & Na_2S & + & 4CO. \\ \text{Sodium} & & \text{Carbon.} & & \text{Sodium} & & \text{Carbon} \\ \text{Sulphate.} & & & & \text{Sulphide.} & & \text{Monoxide.} \end{array}$$

The sodium sulphate is first reduced to sulphide, and the latter reacts with the calcium carbonate, forming calcium sulphide and sodium carbonate :

$$\begin{array}{ccccccc} Na_2S & + & CaCO_3 & = & Na_2CO_3 & + & CaS. \\ \text{Sodium} & & \text{Calcium} & & \text{Sodium} & & \text{Calcium} \\ \text{Sulphide.} & & \text{Carbonate.} & & \text{Carbonate.} & & \text{Sulphide.} \end{array}$$

The above process was formerly carried out in an ordinary reverberatory furnace, but now nearly all works have adopted a revolving furnace, as shown in Fig. 64. The charge is introduced into the cylinder B from cars above, and, after fusion from the heat of the furnace A, is run out into cars beneath. The heat from A is introduced through the axle into the cylinder, and the excess passes out through the other side, to be used as presently described. These revolving furnaces accomplish by mechanical means what was formerly very difficult and costly labor,—namely, thorough mixing of the material during heating. The cylinder is revolved very slowly at first, and finally not faster than one revolution in three minutes. The quantities of the different materials employed by Leblanc were 100 parts each of salt-cake and limestone and 50 parts coal. In some works at the present time this proportion is only varied by using a relatively smaller amount of coal, but in some other manufactories there are employed 142 parts salt-cake, 100 parts limestone, and 24 parts coal.

These revolving furnaces first came into use in 1868. Some of them are large enough to produce a daily yield of 80 to 90 tons of black ash. They are made of wrought iron and lined with fire-brick.

Crude soda or black ash has about the following composition :

	Per cent.
Sodium carbonate	45
Calcium sulphide	30
Calcium oxide	10
Calcium carbonate	5
Foreign matter	10

Considerable quantities of this crude soda are used without further purification in the manufacture of green glassware, in soap-making, and in bleaching.

The next step in the Leblanc process consists in lixiviating the black ash, evaporating the solution, and crystallizing. The black ash is allowed to weather for a short time, by which it becomes more porous and more easily broken into small pieces ; it is then treated with water in such a manner as to effect solution with the least possible amount of liquid. This is accomplished by using a series of vats, in which that ash which is nearly exhausted is treated with fresh water ; the fresh ash being treated by water already partly saturated.

The solution is evaporated in the pans D, D, Fig. 64, by the waste heat from the furnace. The crystals which separate are raked out into E, E. These crystals are sometimes dissolved in water and recrystallized, by which they become crystal soda, or, as is much oftener the case, they are calcined on the hearth of a reverberatory furnace, and become raw soda or soda ash. In the latter process calcium sulphide is converted into calcium sulphate, caustic alkali is carbonated, and all sulphide which causes the yellow color is removed.

The mother liquor from the first crystallization of the soda contains considerable quantities of sodium hydrate ; it also contains some chloride, sulphate, cyanide, and sulphide as impurities. These are in part gotten rid of by allowing the liquor to run down a coke tower in which it meets a current of air ; the latter oxidizes the sulphides and cyanides. The liquor is then concentrated until it has a specific gravity of 1.10, when it is boiled with calcium hydrate, which removes carbonates and sulphates ; after they settle out, the clear liquor is drawn off into an iron vessel, evaporated, and heated to redness, when, after treatment with a little sodium nitrate to remove all cyanides, the caustic alkali is run into iron drums and sent into commerce.

Modifications of the Leblanc Process.—While many suggestions have been made regarding improvements of the Leblanc process, comparatively few have come into use. That devised by Hargreaves and Robinson involves an important change in the preparation of salt-cake. It consists in acting directly on sodium chloride by sulphurous oxide, oxygen (atmospheric), and watery vapor. The reaction is as follows :

$$\underset{\substack{\text{Sulphur}\\\text{Dioxide.}}}{SO_2} + \underset{\text{Oxygen.}}{O} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Sodium}\\\text{Chloride.}}}{2NaCl} = \underset{\substack{\text{Sodium}\\\text{Sulphate.}}}{Na_2SO_4} + \underset{\substack{\text{Hydrochloric}\\\text{Acid.}}}{2HCl.}$$

The sulphur dioxide is furnished directly from iron pyrites by roasting. The result is a purer product at a lower cost, but the increased expense of installation, greater consumption of fuel, and increased outlay for labor have been impediments to its general adoption.

Most of the other changes which have met with favor have related to utilization of the waste materials. These have mostly been in the direction of recovering the sulphur. When we consider that each ton of sodium carbonate produced represents 1½ tons of dry *alkali waste*, it is easily understood that the economical distribution of this waste becomes a serious problem. This waste consists chiefly of calcium sulphide and carbonate, with small quantities of a number of other compounds.

The process of Chance for utilizing the sulphur is probably the most practical one that has been suggested. By it 90 per cent. of the sulphur is recovered, and used as such, or converted into sulphur dioxide, to be used again in the production of sodium carbonate. The process consists in treating the alkali waste with carbon dioxide from the lime-kilns, which are nearly always associated with alkali works. This carbon dioxide has usually been allowed to go to waste. When it, in the presence of moisture, is brought in contact with calcium sulphide, the following reaction takes place, with the formation of calcium sulphydrate and carbonate:

$$\underset{\text{Calcium Sulphide.}}{2CaS} + \underset{\text{Carbon Dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Calcium Carbonate.}}{CaCO_3} + \underset{\text{Calcium Sulphydrate.}}{Ca(SH)_2}.$$

With a further addition of carbon dioxide calcium carbonate is formed, with evolution of hydrogen sulphide, as follows:

$$\underset{\text{Calcium Sulphydrate.}}{Ca(SH)_2} + \underset{\text{Carbon Dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Calcium Carbonate.}}{CaCO_3} + \underset{\text{Hydrogen Sulphide.}}{2H_2S}.$$

This hydrogen sulphide is either burnt to SO_2 and used in the preparation of sulphuric acid, or the quantity of air with which it is heated is regulated so that free sulphur is formed as follows:

$$H_2S + O = H_2O + S.$$

A part of the alkali waste is utilized in the production of sodium thiosulphate, as described under that salt.

4. *The Ammonia-Soda Process.*—As long ago as 1838 this process was patented by Dyer and Hemming, but was first conducted on a commercial scale in 1855 by Schlössing and Rolland near Paris. The numerous practical difficulties, however, were not overcome until Solvay, in 1861, established a manufactory

near Brussels. Since that time it has slowly encroached on the Leblanc process, so that in 1892 the official figures for the output by these processes were as follows:

	Tons.
Leblanc soda	519,593
Ammonia-soda	304,897
Total	824,490

Leblanc soda does not appear to be produced in the United States, except, perhaps, the relatively small amount from the natural sodium sulphate in Wyoming, while the production of ammonia-soda by the Solvay patent amounted to 82,000 tons in 1892.

The ammonia-soda process consists in decomposing a saturated solution of sodium chloride with acid ammonium carbonate as follows:

$$\underset{\substack{\text{Sodium}\\\text{Chloride.}}}{NaCl} + \underset{\substack{\text{Acid}\\\text{Ammonium}\\\text{Carbonate.}}}{NH_4HCO_3} = \underset{\substack{\text{Acid}\\\text{Sodium}\\\text{Carbonate.}}}{NaHCO_3} + \underset{\substack{\text{Ammonium}\\\text{Chloride.}}}{NH_4Cl.}$$

In practice this is effected by running the salt solution down through a column, which meets in its descent the ammonia gas. This apparatus in which the brine is saturated is either iron, tin lined, or wood lined with lead. The ammonia enters through a perforated iron plate, by which it is broken up into small bubbles. Considerable rise of temperature takes place during the absorption, and the saturated brine is passed through a cooler into another vessel, in which it is saturated with the carbon dioxide. The reaction may be summed up as follows:

$$\underset{\substack{\text{Sodium}\\\text{Chloride.}}}{NaCl} + \underset{\text{Ammonia.}}{NH_3} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Acid}\\\text{Sodium}\\\text{Carbonate.}}}{NaHCO_3} + \underset{\substack{\text{Ammonium}\\\text{Chloride.}}}{NH_4Cl.}$$

The ammonia is produced from ammonium chloride and calcium or magnesium oxide. Originally the calcium compound was employed, but by using the magnesium compound magnesium chloride is formed, which may be decomposed by steam with the production of hydrochloric acid and magnesium oxide. The process thus becomes a continuous one, in which the ammonia and magnesia are repeatedly used over, while the fresh materials required are common salt and carbon dioxide; the latter is obtained from the lime-kilns, from magnesite, or from fuel.

The sodium bicarbonate produced in this process is collected on a vacuum filter, washed with a small quantity of cold water, and dried. It is converted into normal carbonate by heat:

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

The carbon dioxide is used to furnish a part of that required to saturate the ammoniacal brine.

5. *Soda from Cryolite.*—The mineral cryolite occurs in enormous deposits in Greenland. The product of these mines is brought to Philadelphia and converted into sodium carbonate and bicarbonate at the works of the Pennsylvania Salt Company in Western Pennsylvania. This mineral has the composition $Al_2F_6.6NaF$, and is therefore a double fluoride of sodium and aluminum. When the finely-divided mineral is mixed with chalk or limestone and heated, the following reaction takes place:

$$\underset{\text{Cryolite.}}{Al_2F_6.6NaF} + \underset{\substack{\text{Calcium}\\\text{Carbonate.}}}{6CaCO_3} = \underset{\substack{\text{Sodium}\\\text{Aluminate.}}}{Al_2O_3.3Na_2O} + \underset{\substack{\text{Calcium}\\\text{Fluoride.}}}{6CaF_2} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{6CO_2}.$$

The fused mass is treated with water, whereby the soluble sodium aluminate is dissolved; carbon dioxide is then passed through this solution under pressure, which precipitates the aluminum hydrate and forms sodium carbonate:

$$\underset{\substack{\text{Sodium}\\\text{Aluminate.}}}{Na_6Al_2O_6} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{3CO_2} + \underset{\text{Water.}}{3H_2O} = \underset{\substack{\text{Sodium}\\\text{Carbonate.}}}{3Na_2CO_3} + \underset{\substack{\text{Aluminum}\\\text{Hydrate.}}}{Al_2(OH)_6}.$$

The clear solution is run off from the precipitate, and the sodium carbonate allowed to crystallize. A considerable portion of this company's output is converted into bicarbonate.

Properties.—When containing its full 10 molecules of water of crystallization, sodium carbonate occurs in large, colorless, monoclinic crystals, which have a specific gravity of 1.440 at 15°. The salt is odorless, and has an alkaline taste and reaction. When exposed to air the crystals become white, and gradually crumble to a fine white powder, losing about one-half of their water of crystallization, amounting to 31.46 per cent. The salt dissolves in 1.6 parts of water at 15°, and in 0.2 part of boiling water; it is most soluble at 38°, 0.09 part of water at that temperature being sufficient to dissolve 1 part of the crystals. The salt is insoluble in alcohol and ether, but soluble in 1.02 parts of glycerin. On the application of heat the crystals melt in their water of crystallization at 32.5°, and at 80° and above they lose all their water, amounting to about 63 per cent. The salt fuses at a bright red heat, or about 814°. When sodium and potassium carbonates are taken in the proportion of their molecular weights, the mixture fuses at a considerably lower temperature than will either singly.

Sodium carbonate is perhaps used in larger quantity and in a greater variety of ways than any other alkaline salt. In addition to being employed itself, it forms the base from which many other sodium salts are prepared.

Pure sodium carbonate is prepared by dissolving the commercial crystals in one-half their weight of water at 30° to 40°, filtering the solution, and allowing it to stand in a cool place. The small crystals which separate are collected in a funnel, allowed to drain well, and then washed with a small quantity of cold water, or with a saturated solution of pure sodium carbonate. It may also be obtained by washing sodium bicarbonate with cold water, drying, and heating the residue to redness.

The impurities in the commercial carbonate are sodium chloride and sulphate, with perhaps ammonium salts.

Dried Sodium Carbonate. **Sodii Carbonas Exsiccatus,** U. S. P.—This is obtained from the commercial crystals by allowing them to effloresce at a temperature not exceeding 25° until they disintegrate, and then drying at 45° until they have lost one-half their weight.

Sodium Bicarbonate (*Acid Sodium Carbonate*). **Sodii Bicarbonas,** U. S. P.—This salt was first prepared by Valentine Rose in 1801.

It occurs in many mineral waters, especially those of Ems and Vichy.

Preparation.—Sodium bicarbonate was originally prepared by passing carbon dioxide into a concentrated solution of neutral sodium carbonate; the bicarbonate, on account of its sparing solubility, separates out:

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3.$$

Since the solution absorbs carbon dioxide slowly, the commercial process consists in making an intimate mixture of 4 parts of the effloresced carbonate and 1 part of the crystals. This mixture is distributed on broad shelves in a room, and carbon dioxide from some cheap source is passed in until the salt is saturated. Large quantities of the bicarbonate are now produced in the ammonia-soda process for making the neutral carbonate, and this furnishes a satisfactory product provided ammonium salts are removed. The cryolite process for the neutral carbonate also furnishes a superior bicarbonate; and these two sources now nearly supply the American markets, since the importations of 20,000,000 pounds annually some twenty years ago have decreased to less than 2,000,000 at the present time.

Properties.—Sodium bicarbonate forms in small monoclinic, tabular crystals, which are frequently united into crusts. As found in the shops, it is a white, opaque powder, permanent in the air under ordinary circumstances, but decomposing slowly in moist air. It has a mildly alkaline taste, and the cold solution, when freshly prepared, gives a faintly alkaline reaction to litmus paper.

The crystals have a specific gravity of 2.22 at 16°. The salt is soluble in 11.3 parts of water at 15°, and at a higher temperature, in the presence of water, it loses carbon dioxide, the neutral carbonate being formed; at the boiling temperature it is entirely converted into the neutral salt. Sodium bicarbonate is insoluble in alcohol and in ether.

On the application of heat, carbon dioxide and water are given off, with the formation of the neutral carbonate, as follows:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

The reaction may be completed at 70°, although it takes place more rapidly at 100°, and when complete there is a loss of 36.3 per cent.

Uses.—Sodium bicarbonate enters into the composition of most baking powders; it is used as a cheap source of carbon dioxide in the preparation of effervescent drinks; and it has considerable use in the textile industries, especially in ungumming silk and scouring wool, as it attacks the fibre less than soap or ammonia.

AMMONIUM.

Formula, NH_4. *Molecular Weight*, 18.01. *Valence*, I.

History.—The salts of ammonium were known to the ancients, but ammonia gas was first collected by Priestley in 1774, although it was previously known that a pungent odor was developed on adding an alkali to sal ammoniac. Berthollet, in 1785, determined it to be composed of nitrogen and hydrogen.

Theoretical Considerations.—The present theory concerning ammonium salts is that the compound NH_4 is a metal-like body which combines with the acids in the same manner that sodium and potassium do. This view has been strengthened by the formation of an amalgam composed of the radical NH_4 and mercury. When ammonium chloride, in contact with mercury, is subjected to the electric current, a bulky, buttery mass is formed which is considered to be ammonium amalgam. The same product is obtained by placing sodium amalgam containing 1 per cen of sodium in a concentrated solution of ammonium chlorid adding at the same time a few fragments of the salt. The bulk amalgam which is formed becomes crystalline at very low temperatures, and at —29° begins to decompose, forming 2 volum of ammonia gas and 1 volume of hydrogen. The salts of ammonium most closely resemble those of potassium, with which the are isomorphous.

Occurrence and Sources.—The salts of ammonium a widely distributed in nature. The carbonate, nitrate, and nitri are found in small quantities in the atmosphere, in rain, and i snow ; the chloride is found in many volcanic gases ; many of th above, as well as other compounds of ammonium, are found i the soil, and in the secretions of plants and animals.

One of the chief inorganic sources of ammonium salts is th native carbonate in the guano deposits of South America ; th salt which exists in this guano is the acid carbonate, NH_4HCO

The suffoni of Tuscany yield, besides boric acid, a considerabl quantity of ammonium sulphate ; in one locality four suffor yield some 1500 kilos of ammonium sulphate in 24 hours. Thi salt is supposed to have resulted from the decomposition of organic matter in the Tuscan mountains, since the soil in the vicinity of the lagoons is impregnated with ammonium sulphate.

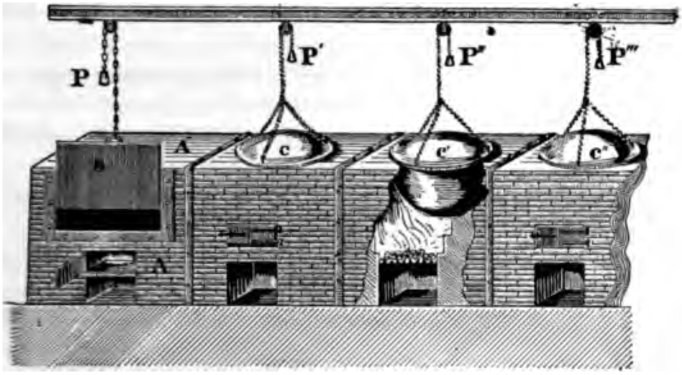
The organic sources of ammonium salts are of the greate importance, and yield nearly all of the commercial salts ; of thes stale urine and the product from the distillation of bones formerl played an important part, but at the present time practically th entire supply comes from gas-liquor, from the condensed gase of coke-ovens and iron-works, and from the watery distillate o shale-works. These various ammoniacal liquors are treated according to the salt required, usually the chloride or sulphate, th details of which will be considered under the respective salts.

HALOGEN SALTS OF AMMONIUM.

Ammonium Chloride, NH_4Cl (Sal Ammoniac). **Ammon Chloridum,** U. S. P.—Sal ammoniac was prepared in earli times in Egypt by the sublimation of the ashes and soot resulti from the burning of camel's dung, which was there used as fu The salt may be prepared by the direct union of equal volum of the gases, ammonia and hydrochloric acid.

At the present time the ammoniacal water from gas-works or similar sources is neutralized with hydrochloric acid, or oftener the ammonia gas is liberated from these liquors by lime and passed into the hydrochloric acid. The salt is first partly purified by crystallization, and then it is sublimed. This operation is usually conducted in cast-iron vessels (Fig. 65) lined with fire-clay, the dome sometimes being of earthenware or glass. The crude salt is rammed in tightly, and then heat is applied, gently at first in order to drive off moisture; a small hole is left in the top of the dome to allow the escape of this moisture. When the cake of sublimed salt in the dome has reached a sufficient thickness,—from 6 to 12 centimeters, according to the size of the caldron,—the dome is raised and the cake removed. When prepared in iron vessels sal ammoniac is usually contaminated with some of that metal; this may be prevented by adding to the charge, before subliming, about 5 per cent. of calcium phosphate, by which means any ferric chloride is decomposed and remains behind as phosphate. The crystalline and granular ammonium chloride is prepared by adding to the powdered salt a hot, saturated solution of the same, so as to form a magma of crystals, which are placed in moulds similar to those used in the manufacture of loaf-sugar; after thorough draining, the whole is dried, and the loaf of the salt is removed and packed for shipment. A former official process consisted in adding to a solution of the salt a little ammonium hydrate, filtering, evaporating, and granulating; this process was for the purpose of removing iron.

FIG. 65.



Sublimation of ammonium chloride.

should not be decomposed when colored, but may be reclaimed by dissolving in water, decolorizing with a small quantity of ammonia water, evaporating and granulating.

AMMONIUM AND SULPHUR.

Ammonium Monosulphide $(NH_4)_2S$.—When 2 volumes of ammonia gas and 1 volume of hydrogen sulphide are mixed at a temperature of —18°, ammonium monosulphide is formed. It forms colorless, glittering crystals, which commence to decompose at ordinary temperatures into ammonia and ammonic sulphydrate. This compound is prepared in aqueous solution by saturating 3 parts of solution of ammonia with hydrogen sulphide and then adding 2 parts of ammonia water. This is the official test-solution. It is a valuable reagent in the laboratory, and is very extensively used.

Ammonium Hydrosulphide, NH_4SH.—This compound is obtained when ammonia gas and hydrogen sulphide are mixed at ordinary temperatures; on cooling to 0°, colorless, acicular crystals separate. These crystals are formed when alcoholic ammonia is saturated with hydrogen sulphide. The compound is formed in aqueous solution when aqueous ammonia is saturated with hydrogen sulphide:

$$NH_4OH + H_2S = NH_4SH + H_2O.$$

This solution and the preceding one of ammonium monosulphide are colored yellow on standing, owing to the formation of the higher ammonium polysulphides and water. There are at least three of these higher sulphides: *ammonium tetrasulphide,* $(NH_4)_2S_4$, obtained by cooling the mother liquor from the pentasulphide and saturating it with ammonia and hydrogen sulphide; *ammonium pentasulphide,* $(NH_4)_2S_5$, prepared by dissolving sulphur in the solution of hydrosulphide; and *ammonium heptasulphide,* $(NH_4)_2S_7$, formed when the pentasulphide is exposed to the air.

OXYGEN SALTS OF AMMONIUM.

Ammonium Sulphate, $(NH_4)_2SO_4$.—This salt is met with as a by-product in the manufacture of boric acid, and is found native as the mineral *mascagnite.* It is prepared by saturating ammoniacal gas-liquor with sulphuric acid, evaporating rapidly, and removing the crystals as they form by perforated ladles. As thus obtained the crystals are of a dark color. They are first allowed to drain well, then dissolved in water, treated with animal charcoal, filtered, and recrystallized.

Properties.—Ammonium sulphate occurs in large, transparent, rhombic crystals, isomorphous with potassium sulphate They are soluble in 1.3 parts of water at 15°, and in 1 part o boiling water, insoluble in absolute alcohol, but slightly solubl in ordinary alcohol. On the application of heat the crystals me

Ammonium Iodide, NH_4I. **Ammonii Iodidum, U. S. P.**—The simplest method of preparing this salt is by neutralizing hydriodic acid with ammonia:

$$NH_4OH + HI = NH_4I + H_2O.$$

Ammonium Hydrate.	Hydriodic Acid.	Ammonium Iodide.	Water.

Hydriodic acid is prepared with some difficulty and expense, so that other methods have been tried with moderate success; in one of these powdered iodine is added to freshly prepared ammonium sulphydrate, forming ammonium iodide, hydrogen sulphide, and sulphur:

$$I_2 + 2NH_4HS = 2NH_4I + H_2S + S.$$

Iodine.	Ammonium Sulphydrate.	Ammonium Iodide.	Hydrogen Sulphide.	Sulphur.

It has been found impossible to remove all sulphur from the iodide in this process.

The following method was official in the U. S. Pharmacopœia of 1870: Concentrated hot solutions of 33 parts potassium iodide and 13 parts ammonium sulphate are mixed, stirred well, mixed with alcohol, and the whole cooled to 40°:

$$2KI + (NH_4)_2SO_4 = 2NH_4I + K_2SO_4.$$

Potassium Iodide.	Ammonium Sulphate.	Ammonium Iodide.	Potassium Sulphate.

The mixture is then thrown into a funnel, previously stopped with cotton, allowed to drain, and the residual potassium sulphate washed with a mixture of 2 volumes of water and 1 volume of alcohol. The filtrate containing the ammonium iodide is then evaporated carefully to dryness, stirring, in order to granulate the salt.

When prepared according to this process ammonium iodide always contains small quantities of ammonium sulphate. The product should be kept in small, well-stopped vials protected from the light.

Properties.—Ammonium iodide occurs in minute, colorless, cubical crystals, odorless, and having a sharp, saline taste. It is soluble at 15° in 1 part of water and in 9 parts of alcohol, in 0.5 part of boiling water and in 3.7 parts of boiling alcohol. When heated, it evolves vapors of iodine and completely volatilizes without melting. Its aqueous solution is neutral to litmus paper.

Ammonium iodide deliquesces when exposed to the air, and gradually decomposes with a yellow color, due to the liberation of free iodine. The colored salt has a faint odor of iodine. It should not be decomposed when colored, but may be reclaimed by dissolving in water, decolorizing with a small quantity of ammonia water, evaporating and granulating.

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Properties.—Ammonium sulphate occurs in large, transparent, rhombic crystals, isomorphous with potassium sulphate. They are soluble in 1.3 parts of water at 15°, and in 1 part of boiling water, insoluble in absolute alcohol, but slightly soluble in ordinary alcohol. On the application of heat the crystals melt at 140° ; at 280° they decompose, with evolution of ammonia, water, and nitrogen ; at the same time ammonium sulphite with some sulphate sublimes.

Uses.—Ammonium sulphate is one of the most useful of the ammonium salts, since it forms the easiest method of recovering the ammonia from gas-liquors, and it is then used as a basis for the preparation of the other ammonium salts. It is especially employed in the manufacture of ammonia-alum and as a fertilizer.

Acid Ammonium Sulphate, NH_4HSO_4, is obtained when the neutral sulphate is crystallized in dilute sulphuric acid.

It forms rhombic crystals which resemble in form those of acid potassium sulphate.

Ammonium Nitrate, NH_4NO_3.—The usual process for obtaining this salt is by saturating nitric acid with ammonium hydrate or carbonate ; a somewhat more economical method consists in mixing solutions of ammonium sulphate and potassium nitrate; the result is double decomposition with the formation of potassium sulphate and ammonium nitrate ; the latter, being much more soluble, is obtained after the potassium sulphate has crystallized out.

Properties.—Ammonium nitrate is found in commerce in long, thin, colorless, rhombic prisms, or in white, fused masses, or as a white, granular powder ; it is odorless, has a sharp, bitter, saline taste, and is somewhat deliquescent. Its aqueous solution is neutral to litmus paper. The salt is soluble at 15° in 0.5 part of water and in 20 parts of alcohol ; it is very soluble in boiling water and in 3 parts of boiling alcohol. It melts at 165°, and between 230° and 250° it is decomposed into nitrogen monoxide and water, as follows :

$$NH_4NO_3 \quad = \quad N_2O \quad + \quad 2H_2O.$$

A small proportion of the salt is sublimed unchanged at the same time. The fused salt acts as an energetic oxidizing agent.

Uses.—Ammonium nitrate is used largely in the production of nitrogen monoxide, or laughing gas. The salt when dissolved in water produces a decided fall in temperature.

Ammonium Nitrite, NH_4NO_2, is formed by decomposing a solution of silver nitrite with ammonium chloride :

$$NH_4Cl \ + \ AgNO_2 \ = \ NH_4NO_2 \ + \ AgCl.$$

The crystals are obtained from this by evaporating the filtrate at ordinary temperatures over sulphuric acid. Ammonium nitrite occurs in indistinctly crystalline masses, which decompose when heated into water and nitrogen.

Normal Ammonium Phosphate, $(NH_4)_3PO_4.3H_2O$, is sometimes found in guano; it is also obtained by mixing a concentrated solution of hydrogen diammonium phosphate with water of ammonia. There are deposited small prismatic or acicular crystals, which decompose when exposed to the air, or when the solution is boiled.

Hydrogen Diammonium Phosphate, $(NH_4)_2HPO_4$, is also found in some guanos, and is prepared by evaporating a solution of phosphoric acid with a slight excess of ammonia. The salt is deposited in transparent monoclinic prisms.

Dihydrogen Ammonium Phosphate, $NH_4H_2PO_4$.—When the phosphoric acid is in slight excess with ammonia, crystals of this compound separate out.

Hydrogen Ammonium Sodium Phosphate, $NaNH_4HPO_4.4H_2O$.—Microcosmic salt occurs in guano and in putrid urine. The salt is prepared by dissolving 5 parts of ordinary sodium phosphate, $Na_2HPO_4.12H_2O$, in hot water, adding to a hot solution of the ordinary ammonium phosphate, $(NH_4)_2HPO_4$, and allowing the solution to cool. The salt separates in transparent, monoclinic, prismatic crystals. They have a distinctly saline taste, and are readily soluble in water. On the application of heat the salt melts, gives off water and ammonia, and leaves a residue of the dihydrogen sodium phosphate; the further application of heat melts this salt to clear liquid with further loss of water, and with the formation of sodium hexametaphosphate, which forms a clear glass on cooling. Because of this property of forming a clear glass the salt is largely used in blowpipe analysis.

Ammonium Carbonate, $NH_4HCO_3.NH_4NH_2CO_2$. **Ammonii Carbonas, U. S.** P.—As will be seen from the above formula, the official salt is a compound of the acid ammonium carbonate with ammonium carbamate. Normal ammonium carbonate, $(NH_4)_2CO_3$, is obtained when the official salt is dissolved in water:

$$\underset{\text{Official Ammonium Carbonate.}}{NH_4HCO_3.NH_4NH_2CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Acid Ammonium Carbonate.}}{NH_4HCO_3} + \underset{\text{Normal Ammonium Carbonate.}}{(NH_4)_2CO_3}.$$

When the normal carbonate is desired in quantity and in a solid form, the official compound is digested for 2 hours at a temperature of 12° with strong aqueous ammonia; the resulting white, crystalline powder is dried by pressing between folds of absorbent paper. These crystals are readily converted into the acid carbonate.

The official, which is also the commercial, salt is prepared by heating in iron retorts ammonium sulphate and calcium carbonate or chalk, with sometimes a small quantity of charcoal:

$$\underset{\text{Ammonium Sulphate.}}{2(NH_4)_2SO_4} + \underset{\text{Calcium Carbonate.}}{2CaCO_3} = \underset{\text{Official Ammonium Carbonate.}}{NH_4HCO_3.NH_4NH_2CO_2} + \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Water.}}{H_2O} + \underset{\text{Calcium Sulphate.}}{2CaSO_4}.$$

After the condensation of the ammonium carbonate, the uncondensed vapors, containing water and ammonia, are led into sulphuric acid in order to recover the ammonia.

Crude ammonium carbonate may also be prepared by passing ammonia, liberated from gas-liquors by lime, into leaden chambers along with carbon dioxide and water.

$$\underset{\text{Ammonia.}}{3NH_3} + \underset{\text{Carbon Dioxide.}}{2CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Official Ammonium Carbonate.}}{NH_4HCO_3.NH_4NH_2CO_2}.$$

Properties.—The official ammonium carbonate occurs in "white, hard, translucent, striated masses, having a strongly ammoniacal odor without empyreuma, and a sharp, saline taste. On exposure to the air, the salt loses both ammonia and carbonic acid, becoming opaque, and is finally converted into friable, porous lumps, or a white powder." The salt is soluble in about 5 parts of water at 15° ; it is decomposed by boiling water, with the elimination of carbonic acid and ammonia, resulting finally, after prolonged boiling, in complete dissipation of the salt. Alcohol dissolves the carbonate, leaving the acid carbonate behind. On the application of heat, ammonium carbonate is completely dissipated without darkening or charring. The aqueous solution reacts alkaline to litmus, and effervesces strongly with acids.

Hydrogen Ammonium Carbonate, NH_4HCO_3. Ammonium Bicarbonate.—Crystals of this salt have been found in Patagonian guano and in the purifiers of gas-works.

When the commercial carbonate is exposed to the air for some time a white powder results, consisting of the bicarbonate; it may also be prepared by passing carbon dioxide into an aqueous solution of the ordinary carbonate. It is usually found as a white, mealy powder, but may be obtained in large rhombic crystals by allowing them to form slowly from aqueous solution. At 60° it is slowly decomposed into ammonia, water, and carbon dioxide. The salt is soluble in 8 parts of water at 15°; it is insoluble in alcohol.

LITHIUM.

Symbol, Li. *Atomic Weight*, 7.01. *Valence*, I.

History.—In 1817, Arfvedson, while working in the laboratory of Berzelius, found a peculiar substance in the mineral *petalite* from the Swedish iron-mines at Utö. The metal was first isolated by Bunsen and Matthiessen in 1855.

Occurrence.—While lithium is not found in large quantities, it is still widely distributed in the three kingdoms. In the mineral kingdom it is found in *petalite*, a silicate of aluminum, sodium, and lithium, to the extent of 2.7 to 3.7 per cent.; in *lepidolite*, a lithia mica, 1.3 to 5.7 per cent.; and in *spodumene*, a silicate of aluminum, sodium, and lithium, 3.8 to 5.6 per cent. It is found in a number of mineral waters, the most notable in the United States being the springs at Gettysburg. In the vegetable kingdom, lithium has been detected in the ash of the vine, of sea-weed, and of tobacco. The animal kingdom contains small quantities of this metal, as shown by its detection in the ashes of blood and milk and in muscular tissue.

Preparation.—In order to obtain metallic lithium, the chloride is first formed. This is accomplished by fusing at the highest temperature of a wind furnace 10 parts of finely-powdered lepidolite, 10 parts of barium carbonate, 5 parts of barium sulphate, and 3 parts of potassium sulphate. The heavy barium compounds settle to the bottom, while potassium and lithium sulphate remain at the top of the fused mass, and are extracted by water. The sulphates are converted into chlorides by the addition of barium chloride, the solution evaporated to dryness, and the lithium chloride separated from the potassium salt by solution in a mixture of absolute alcohol and ether.

The metal is obtained by fusing the chloride in a small porcelain crucible, and decomposing by an electric current from a zinc-carbon battery of from four to six cells. The positive pole is a small piece of gas carbon, while the negative pole is an iron wire the thickness of a knitting-needle. In a few minutes the metal collects around this wire, and when it has attained the size of a pea, and before it becomes so large as to rise to the surface, it is lifted out by a spoon-shaped iron spatula, and cooled under naphtha.

Properties.—Lithium possesses the silver-white lustre of sodium and potassium, but does not tarnish by oxidation so easily as they do. It is the lightest of all known solids, having a specific gravity, according to Bunsen, of 0.5891 to 0.5983. It floats on ordinary petroleum, and can only be preserved under the lightest gasoline.

When heated to 180° lithium melts, and at a higher temperature ignites, and burns with a brilliant red flame. In contact with water it does not oxidize so actively as sodium, as not sufficient heat is evolved to melt it. Most of the acids act on it slowly, but concentrated nitric acid attacks it with explosive violence.

COMPOUNDS OF LITHIUM.

Lithium Chloride, LiCl.—This salt is usually prepared by dissolving the carbonate in hydrochloric acid, or it is made directly from petalite as described under the metal. When the aqueous solution is evaporated slowly over sulphuric acid at ordinary temperatures, the salt is obtained in octohedra. It is very soluble in water, being one of the most deliquescent salts known. It is soluble in alcohol and in a mixture of absolute alcohol and ether. Lithium chloride fuses at a low red heat, and at a higher temperature is slowly volatilized. On evaporating its aqueous solution to dryness, the salt is slightly decomposed, hydrochloric acid being given off, and the residue becoming alkaline.

Lithium Bromide, LiBr. **Lithii Bromidum**, U. S. P.—This salt is obtained by neutralizing hydrobromic acid with lithium carbonate. It occurs as a white, granular, crystalline powder, odorless, and with a sharp, slightly bitter, saline taste, and a neutral reaction. It is soluble in 0.6 part of water at 15°, and in 0.3 part of boiling water, very soluble in alcohol, and soluble in ether. On the application of heat, lithium bromide melts at low redness, and at a higher temperature is slowly volatilized.

Lithium Oxide, Li_2O, is formed when the metal is burned in air. It is prepared by heating the nitrate to redness in a silver basin. It forms a white, crystalline mass, which dissolves in water with the formation of the hydrate, LiOH. The latter behaves in many respects like sodium hydrate, but is less energetic.

Normal Lithium Sulphate, $Li_2SO_4.H_2O$, is formed in the decomposition of petalite, or other lithia mineral, as described under the metal, or dilute sulphuric acid is neutralized with lithium carbonate. It crystallizes in thin monoclinic plates, and is easily soluble in water and in alcohol. The acid salt, $LiHSO_4$, is also known.

Double Potassium and Lithium Sulphate, $KLiSO_4$, is obtained by dissolving the molecular weight of each salt in water, mixing, and allowing to crystallize, when rhombic crystals of the double salt separate out.

Lithium Phosphate, Li_3PO_4, is quite insoluble in water, which gives it some analytical interest, since lithium salts are thereby separated from the other alkaline metals.

Normal Lithium Carbonate, Li_2CO_3. **Lithii Carbonas**, U. S. P.—On account of its sparing solubility in water, this salt differs from the carbonates of sodium and potassium. It rather forms a connecting link between this group of metals and the next, consisting of calcium, strontium, and barium, whose carbonates it resembles.

Lithium carbonate may be prepared by precipitation of a soluble salt, like the sulphate or chloride, with sodium or ammonium carbonate, and boiling. It is, however, prepared from its source, lepidolite, by powdering and heating the mineral and then digesting with sulphuric acid. The mass with the acid is gently heated, and the cooled product extracted with water. The aqueous solution is boiled with milk of lime, by which iron and aluminum are removed; the filtrate from them consists of potassium, sodium, and lithium hydrates, with a small quantity of lime; the latter is removed by evaporating to dryness and dissolving in a small quantity of hot water, by which a solution is obtained containing the hydrates of the alkalies; from this the lithium carbonate is precipitated by boiling with ammonium carbonate.

This may be purified by suspending 1 part of the carbonate in 20 parts of water and effecting solution by saturating with carbon dioxide, which forms the bicarbonate, $LiHCO_3$; after filtering, the solution is boiled, whereby a pure salt is thrown down.

Properties.—Lithium carbonate is a light, white, odorless powder, with an alkaline taste and reaction. It is permanent in the air; soluble in 80 parts of water at 15° and in 140 parts of boiling water, insoluble in alcohol. On the application of a temperature approaching redness, lithium carbonate melts, and gives off some carbon dioxide; when this melted mass cools, it forms a crystalline mass of lithium carbonate and oxide. The carbonate is also somewhat decomposed when its aqueous solution is boiled for a long time, carbon dioxide escaping and lithium hydrate being formed.

Lithium Bicarbonate, $LiHCO_3$, is not known except in aqueous solution.

Uses.—The salts of lithium have come into use chiefly because of the power possessed by the carbonate of dissolving uric acid. The bromide is supposed to have some advantages over the other alkali bromides, because of the relatively smaller proportion of the base present.

RUBIDIUM.

Symbol, Rb. *Atomic Weight*, 85.2. *Valence*, I.

History.—Rubidium was discovered in 1861 by Bunsen and Kirchhoff, by means of the spectroscope.

Occurrence.—It is found in nature, usually along with potassium, in many mineral waters, chiefly those of Dürkheim, in Baden; in some minerals, as *lepidolite* and *petalite*; and in the ashes of some plants. It is widely distributed, but only in small quantity.

Preparation.—Bunsen recommended the saline residue, after the preparation of lithium from lepidolite, as a source for rubidium salts. The rubidium precipitate with platinum is more insoluble than that of potassium; the latter is separated, therefore, by repeated boiling of the mixed platinum precipitates with small quantities of water. The rubidium compound is reduced by hydrogen, when a chloride is obtained, which furnishes a starting-point for the other salts. The metal is obtained by the same process used in preparing potassium,—namely, by distillation of the charred tartrate.

Properties.—Rubidium is a silver-white metal, which has a waxy consistence as low as —10°. Its specific gravity is 1.52, and it melts at 38.5°. Below a red heat it gives off a bluish vapor. When exposed to the air it inflames spontaneously, and when thrown on water acts energetically, decomposing the latter, burning with a violet flame.

SALTS OF RUBIDIUM.

Many of these salts have been prepared, and found to closely resemble those of potassium, with which they are isomorphous.

Their behavior in the colorless flame is very similar to that of potassium, the flame being a trifle redder. The flame spectrum exhibits two characteristic lines in the violet, which forms the most certain means of detecting rubidium salts. Bunsen stated that he could detect 0.002 milligramme by this reaction.

CÆSIUM.

Symbol, Cs. *Atomic Weight*, 132.7. *Valence*, I.

History.—Cæsium, like rubidium, was discovered by Bunsen and Kirchhoff by means of the spectroscope. This occurred in 1860.

Occurrence.—Cæsium is widely distributed in nature, but in small quantity, the largest quantity being in the mineral *pollux*, found in the island of Elba; it was found to contain 32 per cent. of cæsium; this mineral has also been found at Hebron, Maine, under the name of *pollucite*.

Cæsium is also found in many mineral springs, but not in the ashes of plants, as it is claimed that, in the absence of potassium compounds, cæsium acts as a poison towards plant life.

Preparation.—Cæsium does not appear to be so easily prepared as rubidium. Electrolysis of its cyanide has been attended with some success. Fusion of the hydrate with metallic aluminum has been attended with better results.

Properties.—Cæsium is a silver-white, very soft metal, melting at 26.5°, and having a specific gravity of 1.88. It inflames on exposure to the air, and is the most electro-positive metal known.

SALTS OF CÆSIUM.

The salts of this metal closely resemble those of rubidium and potassium. They color the flame still more reddish, form a double salt with platinum, and react similarly with other reagents. The metal was discovered by its characteristic spectrum, which consists of two intense blue lines and one less intense orange-red line.

CHAPTER II.

THE ALKALINE EARTH GROUP.

THE alkaline earth metals are **Calcium, Strontium,** and **Barium**; they resemble the alkalies in part, and still bear some resemblance to the earths like alumina. The hydrates of this group resemble those of the alkalies, although not so soluble in water, but the carbonates, sulphates, and phosphates, unlike those salts of the alkalies, are insoluble in water.

The metals of the alkaline earths possess a distinct lustre and a white or golden-yellow color. They do not change so rapidly when exposed to the air as the metals of the alkali group. The oxides of these metals are white in color, and possess many properties peculiar to the earths. They are not affected by high temperatures, and are not reduced by hydrogen or carbon under these circumstances. The metals are heavier than water, and decompose it at ordinary temperatures, but not so energetically as the alkali metals.

CALCIUM.

Symbol Ca. Atomic Weight [illegible]. *Valence*, II.

History.—The use of lime in mortar for building purposes by the ancients indicates that this substance was well known to them. A description of the process of lime-burning is found in the writings of Dioscorides and of Pliny. Lime and many of its compounds were designated [illegible] by the ancients, and not distinguished from [illegible] other substances possessing this generic name. Towards the middle of the eighteenth century it was found that [illegible] of earths existed, and lime was recognized as a [illegible] of earth.

The metal was first obtained by Davy in 1808 by the electrolysis of [illegible] in the presence of mercury; an amalgam [illegible] when heated, gave off [illegible]. In 1855 Bunsen and [illegible] by the electrolysis of the [illegible]

[illegible] are widely distributed [illegible] most abundant. The [illegible] chalk, marble, and limestone.

stone, in a comparatively pure condition, but many other minerals contain the carbonate as one of the constituents. The most abundant of these is dolomite, a magnesian limestone, which frequently forms whole mountain ranges.

Calcium fluoride or fluor-spar, CaF_2, is found in considerable quantities throughout the globe; the chloride, $CaCl_2$, occurs in sea water and in many mineral springs. The sulphate is found in the anhydrous condition as anhydrite, $CaSO_4$, or in the hydrated form as selenite or gypsum, $CaSO_4.2H_2O$. The phosphate is found, with chloride or fluoride, in apatite and osteolite. Nearly all silicates contain a considerable proportion of calcium. Calcium in some form is a constituent of all plants and animals. If deprived of it they die, since they will admit of the replacement of other elements, like magnesium, to a limited extent only.

Calcium has also been detected in meteorites, in the sun, and in some fixed stars.

Preparation.—The metal calcium is prepared by electrolysis of the fused chloride, or it may be obtained by heating in a closed iron crucible 1 part of sodium with 7 parts of fused calcium iodide. The temperature is first raised to a dull red heat and then to bright redness. It has also been prepared by strongly heating a mixture of 3 parts of calcium chloride, 4 parts of zinc, and 1 part of sodium; an alloy of zinc and sodium results, which is heated in a crucible made of gas-carbon until the zinc volatilizes; the calcium remains in the form of a button.

Properties.—Calcium is a yellow, lustrous, tough, and malleable metal. It is about as hard as gold, and has the specific gravity 1.5778. It does not oxidize readily in dry air, but in moist air it quickly becomes covered with the hydrate, the action gradually extending through the whole mass. Water is decomposed by calcium at ordinary temperatures with violent evolution of hydrogen; the heat developed, however, is not sufficient to inflame the latter. On the application of heat, calcium burns in the air with a very brilliant yellow flame. Dilute nitric acid dissolves the metal with such energy that the latter sometimes inflames, but concentrated nitric acid does not attack it until the temperature is raised to the boiling point of the acid.

CALCIUM AND THE HALOGENS.

Calcium Chloride, $CaCl_2$. **Calcii Chloridum, U. S. P.**—This salt was first prepared by Isaac Hollendus, in the fourteenth century, who designated it by the title *sal ammoniacum fixum*, because he prepared it by heating a mixture of sal ammoniac and lime.

It is found in sea water and in many mineral waters; it also occurs as tachydrite at Stassfurt; this is a compound with magnesium chloride, having the formula $CaCl_2 . 2MgCl_2 . 12H_2O$.

Preparation.—Crude calcium chloride is a by-product in several chemical operations; for example, it is the residue in the preparation of ammonia from ammonium chloride; it is obtained in the preparation of potassium chlorate, in the ammonia-soda process, and in the preparation of carbon dioxide from limestone and hydrochloric acid. For many uses this crude product, which is in aqueous solution, is evaporated to dryness in an iron kettle, and then heated until it melts. The product is sent into commerce for dehydrating purposes as fused calcium chloride.

Purified calcium chloride is made by nearly saturating hydrochloric acid with marble, adding chlorine water to oxidize the iron and manganese compounds, and precipitating these by the addition of a slight excess of milk of lime (calcium hydrate). The clear, filtered solution, which is slightly alkaline, is carefully neutralized with hydrochloric acid. This solution is then evaporated to the crystallizing point or to dryness, according to the uses to which it is to be applied.

Properties.—The crystallized salt occurs in large, hexagonal prisms, having the composition $CaCl_2.6H_2O$. On the application of heat it melts at 29°. These crystals rapidly deliquesce on exposure to the air, forming a thick, oily liquid, formerly known as *oleum calcis*.

When the crystals dissolve in water a considerable fall in temperature takes place. A temperature of —48° is obtained by mixing 1½ parts of the crystals with 1 part of snow. When heated to 200°, or when kept for some time over concentrated sulphuric acid, the crystals lose 4 molecules of water of crystallization, a white powder resulting, which possesses energetic dehydrating properties. Above 200° the remaining 2 molecules of water are driven off, and at 720° the salt becomes anhydrous.

The official salt is directed to be "calcium chloride, rendered anhydrous by fusion at the lowest possible temperature." It is described as occurring in "white, slightly translucent, hard fragments, odorless, having a sharp, saline taste, and very deliquescent."

The anhydrous salt is soluble in 1.5 parts of water, and in 8[illegible] parts of alcohol at 15°, in 1.5 parts of boiling alcohol, and very [illegible] freely soluble in boiling water ; it is insoluble in ether. Since the aqueous solution is used for maintaining a temperature above that of boiling water, it is useful to know the boiling point of such a solution ; that containing 50 parts of the anhydrous salt in 100 of water boils at 112°, that containing 200 per cent. of the salt boils at 158°, and that containing 325 per cent. boils at 180°.

The pure salt dissolves in water without residue, and has a neutral reaction. If, however, it be kept at or above the fusing point for some time, a slight decomposition takes place, so that it leaves a residue insoluble in water, and the solution has a faintly alkaline reaction.

Uses.—Calcium chloride has some use in the laboratory as a reagent, but its chief value is as a desiccating agent, in the drying of gases, and in the concentration of liquids. Its solution is valuable, as above stated, for use in water-baths, where it is desired to maintain a constant temperature above that of boiling water.

Calcium Bromide, $CaBr_2$. **Calcii Bromidum,** U. S. P.—Like the preceding salt, calcium bromide is found in certain mineral waters.

It is prepared by neutralizing hydrobromic acid with marble, adding bromine water to oxidize iron and manganese compounds, and precipitating these by the addition of a slight excess of milk of lime. The solution is filtered, and the filtrate carefully neutralized with hydrobromic acid. The resulting solution is then evaporated to dryness and carefully heated to 680°, whereby an anhydrous salt is obtained.

The Pharmacopœia directs that the anhydrous salt be employed. In this state it occurs as white, granular, very deliquescent salt, without odor, and with a sharp, saline taste. At 15° it is soluble in 0.7 part of water, and in 1 part of alcohol ; at the boiling point these liquids dissolve it freely. At 680° the salt melts, above that temperature it is slowly decomposed with loss of bromine. The aqueous solution is neutral to litmus paper.

Uses.—The principal use of this salt is in medicine. It is supposed to have some advantages over the other bromides.

Calcium Iodide, CaI_2, is prepared like the bromide, which it resembles in many particulars. Both salts are so extremely deliquescent that considerable care is necessary in order to keep them in the solid state.

Calcium Fluoride, CaF_2, under the name of fluor-spar, occurs quite abundantly in nature. It is found especially in the limestone caves of the Castleton Valley in Derbyshire, England ; considerable quantities are also found in Saxony. It occurs in cubes and octohedra, and in some other forms belonging to the regular system.

It is also found in the ashes of some plants, in bones, in the enamel of the teeth, and in sea water and mineral springs.

In the pure condition calcium fluoride is colorless, but it is much oftener of a violet, blue, red, green, or brown color, owing to the presence of small quantities of impurities. At a red heat calcium fluoride fuses without decomposition; while hot it phosphoresces in the dark.

Fluor-spar is extensively employed as a flux in many metallurgical operations, and the finer masses of crystals are made into vases and other ornaments.

CALCIUM AND OXYGEN.

Calcium Monoxide, CaO. **Calx**, U.S.P.—Lime is prepared by heating calcium carbonate. If a pure carbonate is used a correspondingly pure product results. In a small way this is accomplished by heating calc-spar or a pure marble in a crucible with a hole in the bottom in order that the furnace gases may pass through and carry off the carbon dioxide.

$$\underset{\text{Calcium Carbonate.}}{CaCO_3} = \underset{\text{Calcium Oxide.}}{CaO} + \underset{\text{Carbon Dioxide.}}{CO_2}.$$

On a commercial scale lime-kilns are used. These were formerly constructed so as to be filled with limestone and fuel in alternate layers. Fire was then started at the bottom, and the temperature regulated by the air-supply below. Such a furnace, however, could only be emptied when cool. At the present time continuous furnaces are much more used. Such a one is shown in Fig. 66. It is built on the slope of a hill, so as to bring the door at the top on a level with the ground to facilitate the introduction of the limestone. The heat is supplied by two fires, F, F, the finished product is removed at D, Fig. 67. Fig. 66 shows a section cut parallel with the side of the hill, while Fig. 67 shows a section cut at right angles to this, by which the draw-hole D is shown. These furnaces are used in the well-known lime districts of Chester Valley, near Philadelphia. At the ordinary pressure of the atmosphere, a temperature of 812° is required for the dissociation of limestone, but in practice a temperature of 925° is usually employed. If the limestone contain much magnesia it is liable to sinter and form a semi-fused mass, so that in burning this variety a lower heat must be maintained. Coal is the chief fuel used at the present time, although formerly much wood was employed.

Properties.—Pure lime occurs in white, amorphous masses. It often contains iron, and consequently is of a grayish or yellowish shade of color. When exposed to the air it gradually absorbs moisture and carbon dioxide, and crumbles to a white powder. Lime is without odor, but has a sharp, caustic taste. It is soluble in about 750 parts of water at the ordinary temperatures, and in 1300 parts of boiling water; insoluble in alcohol. It is not affected by the highest degrees of heat, but the oxyhydrogen flame causes it to emit an intense white light.

When lime is treated with about one-third its weight of water, added drop by drop, it gradually becomes hot, swells to about twice its bulk, and then falls to a white powder.

The solubility and some of the other properties of lime are closely associated or identical with those of calcium hydrate, since, in the presence of water, the oxide is first converted into hydrate.

FIG. 66.

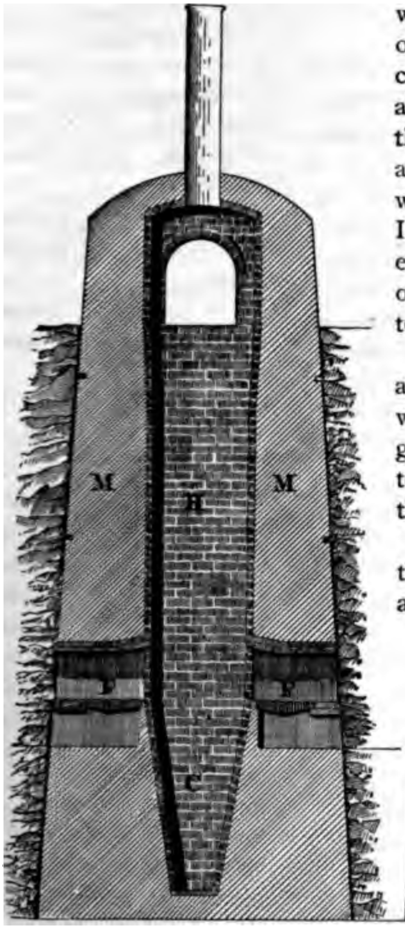
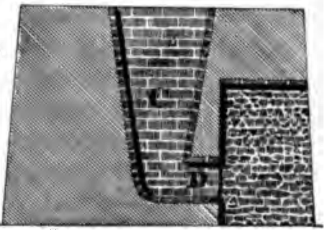


FIG. 67.



Lime-kiln.

Calcium Hydrate, Ca(OH)$_2$, *Calcium Hydroxide.*—When lime is treated with one-third its weight of water, as stated above, the product is calcium hydrate. Considerable heat is developed in this operation: where the proportions are carefully adjusted a temperature of 150° is easily attained. The reaction involved in the formation of the hydrate is as follows:

$$CaO + H_2O = Ca(OH)_2.$$

The resulting product is a fine, white, impalpable powder. Its solution in water forms **Liquor Calcis,** U. S. P., or lime water. This solution has a saline and somewhat caustic taste and an alkaline reaction. On boiling it becomes turbid, owing to the lesser solubility of the hydrate in hot than in cold water. When the clear solution is exposed to the air, a pellicle forms on the surface, due to the formation of calcium carbonate, resulting from the absorption of carbon dioxide from the atmosphere. Calcium hydrate may be obtained by adding sodium or potassium hydrate to a concentrated solution of calcium chloride.

Crystals of calcium hydrate, in the form of tablets or small prisms, may be obtained by evaporating the clear solution of lime water in a vacuum over sulphuric acid.

Milk of lime is a mixture of calcium hydrate and water. It may be made of any desired strength by agitating the freshly-slaked lime with water.

Uses.—Calcium oxide, and therefore also the hydrate, is largely used as a laboratory reagent. The oxide finds much use as a desiccating agent for gases. The hydrate is considerably employed in medicine. The hydrate is largely used in the manufacture of mortar.

Mortars and Cements.—When freshly slaked lime of the consistence of paste is mixed with an equal volume of water, and then 3 to 4 times as much sand is added as there was lime employed, the result is mortar.

The process of hardening which mortar undergoes is called "setting." This setting is sufficiently complete in a few days to give stability to a structure in which it is employed, but the hardening process continues for years. The peculiar action of mortar appears to be due to loss of water and subsequent absorption of carbon dioxide, rather than to the formation of calcium silicate. The value of a mortar depends to a great degree upon the thorough mixing of the ingredients in the process of manufacture. The nature of hydraulic cements will be explained under "Clays" in the section on alumina.

Calcium Dioxide, CaO_2, is prepared by precipitating lime water with hydrogen dioxide. This precipitate has the composition **$CaO_2.8H_2O$;**

it is crystalline, the crystals being in quadratic tables or prisms; they are almost insoluble in water and insoluble in alcohol. The crystals effloresce when exposed to the air, and at 130° lose all their water, becoming anhydrous; at higher temperatures they give off half of their oxygen without undergoing fusion.

OXYGEN SALTS OF CALCIUM AND THE HALOGENS.

Calcium Hypochlorite, $Ca(OCl)_2$, is prepared in a state of purity with great difficulty; a commercial preparation in which it enters is well known, however, as **Calx Chlorata**, U. S. P., or *chlorinated lime*, *chloride of lime*, *bleaching powder*, *bleach*, etc.

Chlorinated lime was first prepared on a commercial scale by Tennant, of Glasgow, in 1798. By some it is considered to be calcium chloro-hypochlorite, having the formula $Ca(OCl)Cl$, by others it is thought to be a mixture of calcium hypochlorite with calcium chloride, having the formula $Ca(ClO)_2CaCl_2.2H_2O$, and containing variable quantities of calcium hydrate. The former view, first proposed by Odling, seems to have been most generally adopted.

Preparation.—This important substance is prepared in enormous quantities in conjunction with alkali works. The chlorine is derived from the waste hydrochloric acid of the Leblanc process, or from the decomposition of magnesium chloride by steam in the ammonia-soda process (see pages 133 to 136). The lime is a finely powdered and sifted dry calcium hydrate. It is placed in chambers of stone, or iron covered with asphalt, to the depth of 4 or 5 inches. The chambers are usually 60 feet long, 18 feet wide, and 7 feet high. They are filled with chlorine and allowed to remain closed for about two days, when the gas is absorbed, and they are opened and the powder is turned. Chlorine is again run in and allowed to remain for another period of two days, when it is usually found that the lime contains from 36 to 37 per cent. of available chlorine. Occasionally a third absorption is resorted to, but this is not often necessary, except in hot weather, when the reaction is less rapid. Usually a series of these chambers are located near together so that the excess of chlorine may be passed from one to the other. In some other cases a series of shelves are arranged in a single chamber, and the contents of each shelf are removed as saturation is completed.

The reaction involved in the production of bleaching powder is considered to be as follows:

[illegible]

$$\underset{\substack{\text{Calcium}\\\text{Hydrate.}}}{Ca(OH)_2} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\substack{\text{Calcium}\\\text{Chloro-hypochlorite.}}}{CaOCl_2} + \underset{\text{Water.}}{H_2O.}$$

Properties.—Chlorinated lime is officially described as "a white, or grayish-white, granular powder, exhaling the odor of hypochlorous acid, having a repulsive, saline taste, and becoming moist and gradually decomposing on exposure to air."

It is only partly dissolved by water or alcohol; the aqueous solution first colors red litmus paper blue, and then bleaches it. It is decomposed by weak acids with evolution of chlorine, and at elevated temperatures dry carbon dioxide will decompose it.

The Pharmacopœia requires that chlorinated lime shall contain not less than 35 per cent. of available chlorine. Much of it comes in commerce packed in sealed paper boxes, coated on the inside with a water-proof material, so that the powder maintains its original strength satisfactorily until opened. In moist air it rapidly deteriorates when exposed.

Calcium hypochlorite may be obtained in crystals by allowing an aqueous solution of chlorinated lime to evaporate in a vacuum over sulphuric acid; these have the composition $Ca(OCl)_2.4H_2O$, and very readily decompose. The fact that the hypochlorite is present in aqueous solution is explained by the supposition that calcium chloro-hypochlorite is decomposed by water as follows:

$$\underset{\substack{\text{Calcium}\\\text{Chloro-hypochlorite.}}}{2CaOCl_2} = \underset{\substack{\text{Calcium}\\\text{Chloride.}}}{CaCl_2} + \underset{\substack{\text{Calcium}\\\text{Hypochlorite.}}}{Ca(OCl)_2.}$$

The chloro-hypochlorite is acted on by acids with the production of chlorine according to the following:

$$\underset{\substack{\text{Calcium}\\\text{Chloro-hypochlorite.}}}{CaOCl_2} + \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{H_2SO_4} = \underset{\substack{\text{Calcium}\\\text{Sulphate.}}}{CaSO_4} + \underset{\text{Water.}}{H_2O} + \underset{\text{Chlorine.}}{Cl_2.}$$

On this last reaction depends the value of chlorinated lime in the bleaching industry.

The process of bleaching by free chlorine is one of oxidation; it combines with hydrogen to form hydrochloric acid, while the liberated oxygen in the nascent state readily attacks coloring matters, water and a colorless compound resulting.

Uses.—Chlorinated lime is used most extensively for bleaching purposes; it is very largely employed as a disinfecting agent, and is undoubtedly one of the best substances for this purpose. Where chlorine is desired in the free state chlorinated lime forms one of the most convenient and economical means of obtaining it.

the simple addition of a dilute acid being sufficient to produce it in liberal quantity, according to a reaction given above.

Calcium Chlorate, $Ca(ClO_3)_2$, is prepared by passing chlorine into hot milk of lime, or solutions of calcium silicofluoride and potassium chlorate are mixed, when potassium silicofluoride crystallizes out, leaving the calcium chlorate in solution, and the latter is crystallized from the very concentrated solution. Calcium chlorate is a very deliquescent salt, and is crystallized with considerable difficulty. The crystals contain 2 molecules of water of crystallization.

Calcium Bromate, $Ca(BrO_3)_2.H_2O$, and *Calcium Iodate*, $Ca(IO_3)_2.6H_2O$, are also known.

CALCIUM AND SULPHUR.

Calcium Monosulphide, CaS.—In 1750 Marggraf noticed that this substance had the property of remaining luminous in the dark after it had been exposed to bright light. It is obtained by heating calcium sulphate with powdered charcoal, or it may be prepared by leading the vapor of carbon disulphide and carbon dioxide over incandescent lime.

Calx Sulphurata, U. S. P. (Sulphurated Lime), is a crude calcium sulphide, prepared by taking 70 parts of dried calcium sulphate, 10 parts of charcoal, and 2 parts of starch. The ingredients are mixed thoroughly, packed in a loosely covered crucible, and heated to bright redness until the mass loses its black color. After the crucible cools the product should be reduced to a fine powder, and at once transferred to small, glass-stoppered vials.

The pure calcium sulphide occurs in white masses. The official product is described as "a pale gray powder, exhaling a faint odor of hydrogen sulphide, having a nauseous, alkaline taste, and gradually decomposed by exposure to air. Very slightly soluble in cold water, more readily in boiling water, which partially decomposes it; insoluble in alcohol."

Sulphurated lime is decomposed by dilute acids with evolution of hydrogen sulphide, even acetic acid being sufficiently strong to effect this change.

It has the property of being phosphorescent in the dark, giving out a greenish, bluish, or violet light, according to the method by which it was prepared.

It has some use in medicine, and may be employed to furnish arsenic-free hydrogen sulphide.

Calcium Sulphydrate, $Ca(SH)_2$, is prepared by saturating milk of lime with hydrogen sulphide:

$$\underset{\substack{\text{Calcium}\\\text{Hydrate.}}}{Ca(OH)_2} + \underset{\substack{\text{Hydrogen}\\\text{Sulphide.}}}{2H_2S} = \underset{\substack{\text{Calcium}\\\text{Sulphydrate.}}}{Ca(SH)_2} + \underset{\text{Water.}}{2H_2O}.$$

It is known only in solution, and is employed as a depilatory.

Calcium Disulphide, CaS_2, is obtained in yellow crystals when milk of lime is boiled with an excess of sulphur, and the filtered solution allowed to cool. These crystals contain 3 molecules of water of crystallization.

OXYGEN SALTS OF CALCIUM AND SULPHUR.

Calcium Sulphite, $CaSO_3$, is precipitated when solutions of calcium chloride and sodium sulphite are mixed. It occurs as a white powder, soluble in 800 parts of cold water. This salt is obtained in crystals by allowing its solution in sulphurous acid to stand exposed to the air; they have the composition $CaSO_3.2H_2O$. A solution of this salt in excess of sulphurous acid is found in commerce under the name of *bisulphite of lime;* it is made by passing sulphur dioxide into milk of lime. It has extensive use as a preservative agent, especially among brewers. Calcium sulphite is employed as a preservative by cider-makers.

Calcium Sulphate, $CaSO_4$, *Gypsum.*—This compound was known to the ancients as a chalk-like substance; likewise the property which the dried gypsum possesses of hardening when moistened with water. Marggraf determined its composition in 1780.

Calcium sulphate is found native as anhydrite associated with limestone, or crystallized with 2 molecules of water as selenite. Two other varieties of this compound are known as satin spar or fibrous gypsum, and crystalline gypsum or alabaster.

This salt may be prepared by treating calcium carbonate, marble, or limestone with sulphuric acid; it is, however, rarely manufactured in this way, because of the abundance of it native, and because it is a by-product in so many chemical processes.

Calcii Sulphas Exsiccatus, U. S. P., is prepared by carefully drying the native gypsum until it loses three-fourths of its water; it then contains about 95 per cent. by weight of calcium sulphate and 5 per cent. of water. The native compound has a specific gravity of 2.31, and it may be deprived of its water at a temperature of 110°–120°. When thus dried it is commercially known as *burnt gypsum*, or *plaster of Paris*. If overheated—that is, above 200°—it will not take up water so readily, and will not harden.

Properties.—The official compound is described as "a fine, white powder, without odor or taste. From moist air it attracts water, becomes granular, and then loses the property of hardening with water. When mixed with half its weight of water, Dried Calcium Sulphate forms a smooth, cohesive paste, which rapidly hardens. It is soluble in about 410 parts of water at 15°, in 388 parts at 38°, and in 476 parts at 100°. In alcohol it is insoluble. It readily dissolves in dilute nitric or hydrochloric acid, also in saturated solutions of potassium nitrate, sodium hyposulphite, and of various ammonium salts." When calcium sulphate is dissolved in hot hydrochloric or nitric acid and the solution is allowed to cool, it separates in glittering, silky, acicular crystals. On heating the salt with sulphuric acid to 100°, it is changed to a porous mass, of which a part dissolves and separates out again on cooling.

Uses.—Gypsum is used in large quantities as a fertilizer; it has some use as a cement, is employed somewhat in surgery, and is the material employed in making plaster casts and certain kinds of ornamental work. The artificially prepared salt, made by precipitating a concentrated solution of calcium chloride with dilute sulphuric acid, is used as a filling for writing-paper under the name of *pearl hardening* or *annaline.*

Calcium Potassium Sulphate, $CaSO_4K_2SO_4.H_2O$. — When intimate mixtures of equal weights of the anhydrous salts are stirred into less than their weight of water, the mass hardens almost immediately; by varying the proportion of water, different qualities of the solidified compound may be obtained. This mixture when used for plaster casts yields a material which possesses a polished surface.

Calcium Sodium Sulphate, $CaSO_4Na_2SO_4$, is found native as a mineral under the name of glauberite. The artificially prepared compound does not possess the same property of setting that the calcium and potassium compound does.

Calcium Thiosulphate, $CaS_2O_3.6H_2O$, is made by warming a mixture of calcium sulphate, sulphur, and water. It forms oblique, six-sided prisms, which are soluble in their own weight of water. The solution is decomposed at a temperature of 60°, sulphur separating.

OXYGEN SALTS OF CALCIUM AND NITROGEN.

Calcium Nitrate, $Ca(NO_3)_2$, occurs as an efflorescence on walls of stables and other places where organic matter is undergoing decomposition. It is abundant in some soils, especially that of nitre plantations.

Calcium nitrate is prepared by dissolving chalk or marble in nitric acid. The anhydrous compound is formed under ordinary circumstances, but when the aqueous solution is allowed to evaporate very slowly over sulphuric acid, crystals are formed containing 4 molecules of water of crystallization. It is a very deliquescent salt, soluble in both water and alcohol. It is sometimes known as *lime saltpetre* or *wall saltpetre.* This salt was formerly used in the preparation of ordinary saltpetre, but has little use at the present time.

OXYGEN SALTS OF CALCIUM AND PHOSPHORUS.

Calcium Phosphate, $Ca_3(PO_4)_2$. **Calcii Phosphas, U. S. P.**—The salt of this formula is also known as ***normal calcium orthophosphate*** and *bone phosphate.* It is found native with calcium fluoride in the minerals apatite and phosphorite. The minerals osteolite and sombrerite are impure calcium phosphates. By far the most extensive occurrence of calcium phosphate is in what is known as the phosphate rock of South Carolina, Florida, and other parts of the Southern United States; it is also found in Canada. This rock frequently contains as much as 90 per cent. of calcium phosphate. Bones are largely composed of calcium phosphate; when burned, they contain from 80 to 85 per cent. of it.

Preparation.—Calcium phosphate is prepared by adding calcium chloride and ammonium hydrate to sodium phosphate:

$$\underset{\substack{\text{Calcium}\\\text{Chloride.}}}{3CaCl_2} + \underset{\substack{\text{Ammonium}\\\text{Hydrate.}}}{2NH_4OH} + \underset{\substack{\text{Sodium}\\\text{Phosphate.}}}{2(Na_2HPO_4.12H_2O)} = \underset{\substack{\text{Calcium}\\\text{Phosphate.}}}{Ca_3(PO_4)_2} +$$

$$\underset{\substack{\text{Ammonium}\\\text{Chloride.}}}{2NH_4Cl} + \underset{\substack{\text{Sodium}\\\text{Chloride.}}}{4NaCl} + \underset{\text{Water.}}{26H_2O.}$$

Properties.—Calcium phosphate precipitates in the above reaction as a white, amorphous powder; it is odorless and tasteless, and permanent in the air. It is almost insoluble in cold water; decomposed by boiling water into an insoluble basic salt, and a soluble acid salt which dissolves. This reaction takes place very slowly in the presence of cold water, so that an exact determination of the solubility of calcium phosphate is impossible. It is readily soluble in solutions of ammonium salts, sodium nitrate, sodium chloride, and a number of other salts; solution of carbonic acid also has some solvent action upon it. At an intense white heat the salt fuses without decomposition.

Uses. Calcium phosphate has some use in medicine, but th[illegible] [illegible]at is insignificant compared with the extent and value of its application as a fertilizer. The phosphate industry commenced in South Carolina, in 1867, with the shipment of 6 tons; there are now over half a million tons annually shipped from that State alone, while North Carolina and Florida produce sufficient to make the total shipments from the three States for 1893, 981,340 tons, valued at $3,434,690.

Dicalcium Orthophosphate, $Ca_2H_2(PO_4)_2$, or *Hydrogen Calcium Orthophosphate*, $CaHPO_4$.—This compound is precipitated when a solution of sodium phosphate is added to one of calcium chloride; it is a white, crystalline powder, containing 2 molecules of water of crystallization. Urinary concretions and deposits are made up largely of this phosphate.

Tetrahydrogen Calcium Phosphate, $CaH_4(PO_4)_2$, is prepared by dissolving either of the preceding phosphates in phosphoric acid and allowing the solution to evaporate spontaneously. This compound is also known sometimes as calcium superphosphate. What is commercially known as *superphosphate of lime* is a mixture of this compound and calcium sulphate, and is prepared by treating bones or phosphate rock with two-thirds of their weight of sulphuric acid. The product is extensively employed as a fertilizer.

Calcium Hypophosphite, $Ca(H_2PO_2)_2$. **Calcii Hypophosphis, U. S. P.**—This salt is prepared by taking 1 part of finely-divided phosphorus and 2 parts of calcium oxide which has been slaked with 1 part of water and then stirred with sufficient water to make a thin mixture.

These ingredients are mixed, placed in a well-ventilated position, and warmed to 40° until combination is complete, or until hydrogen phosphide ceases to be evolved:

$$\underset{\substack{\text{Calcium}\\ \text{Hydrate.}}}{3Ca(OH)_2} + \underset{\substack{\text{Phos-}\\ \text{phorus.}}}{2P_4} + \underset{\text{Water.}}{6H_2O} = \underset{\substack{\text{Calcium}\\ \text{Hypophosphite.}}}{3Ca(H_2PO_2)_2} + \underset{\substack{\text{Hydrogen}\\ \text{Phosphide.}}}{2PH_3}.$$

When the reaction is ended the mixture is filtered and the calcium hydrate removed from the filtrate by carbon dioxide. It is again filtered, and the clear filtrate evaporated at a low temperature in a vacuum over sulphuric acid until crystallization takes place.

The finely-divided phosphorus is obtained by placing 1 part of phosphorus in a flask with 2 parts of powdered glass and 5 parts of water, applying a gentle heat until the phosphorus is melted, and then agitating until cold. By this means the phosphorus is obtained in small particles which more readily combine with the calcium hydrate. Instead of crystallizing the salt from its aqueous solution, it may be precipitated by the addition of alcohol.

Properties.—Calcium hypophosphite occurs in small, water-free, transparent, monoclinic prisms. It is also found in lustrous taining 4 molecules of water of crystallization. It is a very deliquescent salt, soluble in both water and alcohol. It is sometimes known as *lime saltpetre* or *wall saltpetre.* This salt was formerly used in the preparation of ordinary saltpetre, but has little use at the present time.

OXYGEN SALTS OF CALCIUM AND PHOSPHORUS.

Calcium Phosphate, $Ca_3(PO_4)_2$. **Calcii Phosphas,** U. S. P.—The salt of this formula is also known as *normal calcium orthophosphate* and *bone phosphate.* It is found native with calcium fluoride in the minerals apatite and phosphorite. The minerals osteolite and sombrerite are impure calcium phosphates. By far the most extensive occurrence of calcium phosphate is in what is known as the phosphate rock of South Carolina, Florida, and other parts of the Southern United States; it is also found in Canada. This rock frequently contains as much as 90 per cent. of calcium phosphate. Bones are largely composed of calcium phosphate; when burned, they contain from 80 to 85 per cent. of it.

Preparation.—Calcium phosphate is prepared by adding calcium chloride and ammonium hydrate to sodium phosphate:

$$\underset{\text{Calcium Chloride.}}{3CaCl_2} + \underset{\text{Ammonium Hydrate.}}{2NH_4OH} + \underset{\text{Sodium Phosphate.}}{2(Na_2HPO_4.12H_2O)} = \underset{\text{Calcium Phosphate.}}{Ca_3(PO_4)_2} +$$

$$\underset{\text{Ammonium Chloride.}}{2NH_4Cl} + \underset{\text{Sodium Chloride.}}{4NaCl} + \underset{\text{Water.}}{26H_2O.}$$

Properties.—Calcium phosphate precipitates in the above reaction as a white, amorphous powder; it is odorless and tasteless, and permanent in the air. It is almost insoluble in cold water; decomposed by boiling water into an insoluble basic salt, and a soluble acid salt which dissolves. This reaction takes place very slowly in the presence of cold water, so that an exact determination of the solubility of calcium phosphate is impossible. It is readily soluble in solutions of ammonium salts, sodium nitrate, sodium chloride, and a number of other salts; solution of carbonic acid also has some solvent action upon it. At an intense white heat the salt fuses without decomposition.

Uses.—Calcium phosphate has some use in medicine, but that is insignificant compared with the extent and value of its application as a fertilizer. The phosphate industry commenced in South Carolina, in 1867, with the shipment of 6 tons; there are now over half a million tons annually shipped from that State alone, while North Carolina and Florida produce sufficient to make the total shipments from the three States for 1893, 981,340 tons, valued at $3,434,690.

Dicalcium Orthophosphate, $Ca_2H_2(PO_4)_2$, or *Hydrogen Calcium Orthophosphate*, $CaHPO_4$.—This compound is precipitated when a solution of sodium phosphate is added to one of calcium chloride; it is a white, crystalline powder, containing 2 molecules of water of crystallization. Urinary concretions and deposits are made up largely of this phosphate.

Tetrahydrogen Calcium Phosphate, $CaH_4(PO_4)_2$, is prepared by dissolving either of the preceding phosphates in phosphoric acid and allowing the solution to evaporate spontaneously. This compound is also known sometimes as calcium superphosphate. What is commercially known as *superphosphate of lime* is a mixture of this compound and calcium sulphate, and is prepared by treating bones or phosphate rock with two-thirds of their weight of sulphuric acid. The product is extensively employed as a fertilizer.

Calcium Hypophosphite, $Ca(H_2PO_2)_2$. **Calcii Hypophosphis, U. S. P.**—This salt is prepared by taking 1 part of finely-divided phosphorus and 2 parts of calcium oxide which has been slaked with 1 part of water and then stirred with sufficient water to make a thin mixture.

These ingredients are mixed, placed in a well-ventilated position, and warmed to 40° until combination is complete, or until hydrogen phosphide ceases to be evolved:

$$\underset{\text{Calcium Hydrate.}}{3Ca(OH)_2} + \underset{\text{Phosphorus.}}{2P_4} + \underset{\text{Water.}}{6H_2O} = \underset{\text{Calcium Hypophosphite.}}{3Ca(H_2PO_2)_2} + \underset{\text{Hydrogen Phosphide.}}{2PH_3}.$$

When the reaction is ended the mixture is filtered and the calcium hydrate removed from the filtrate by carbon dioxide. It is again filtered, and the clear filtrate evaporated at a low temperature in a vacuum over sulphuric acid until crystallization takes place.

The finely-divided phosphorus is obtained by placing 1 part of phosphorus in a flask with 2 parts of powdered glass and 5 parts of water, applying a gentle heat until the phosphorus is melted, and then agitating until cold. By this means the phosphorus is obtained in small particles which more readily combine with the calcium hydrate. Instead of crystallizing the salt from its aqueous solution, it may be precipitated by the addition of alcohol.

Properties.—Calcium hypophosphite occurs in small, water-free, transparent, monoclinic prisms. It is also found in lustrous scales, or in a fine, white powder. It is odorless, has a nauseous, bitter taste, and is permanent in the air.

The salt is soluble in 6.8 parts of water at 15° and in [illegible] parts of boiling water; it is insoluble in alcohol.

On the application of heat calcium hypophosphite decrepitates, and above 300° it begins to decompose, giving off water, hydrogen, and hydrogen phosphide, and leaving a residue of calcium pyrophosphate and metaphosphate with some red phosphorus. The aqueous solution is neutral to litmus paper.

Uses.—Calcium hypophosphite has considerable use in medicine, and at the same time furnishes a convenient salt from which to prepare the other hypophosphites.

CALCIUM AND SILICA.

Calcium Silicate, $CaSiO_3$.—The compound of this formula occurs native as the mineral wollastonite; okenite, gyrolite, and xonotlite are [illegible] compounds of this. Most natural silicates contain more or less calcium silicate. The compound may also be obtained by adding calcium chloride to a solution of sodium silicate, when it forms a gelatinous precipitate.

Calcium silicate enters into the composition of many varieties of glass.

OXYGEN SALTS OF CALCIUM AND CARBON.

Calcium Carbonate, $CaCO_3$, **Calcii Carbonas Precipitatus.** U. S. P.—In the form of chalk, limestone, and marble this compound occurs in nature so abundantly that whole mountain ranges are formed of it. It is also the chief constituent of egg-shells, of the shells of mollusks, and of coral. In chalk it is amorphous, in marble it is in crystalline masses, while in calcite and aragonite it occurs in distinct crystals. These two minerals illustrate its dimorphous character. Calcite, or calc-spar, has a specific gravity of [illegible] to [illegible], and crystallizes in hexagonal prisms, while aragonite has a specific gravity of 2.92 to 3.28, and occurs in the form of rhombic prisms. When carbon dioxide in small quantity is passed into cold lime water, the precipitate is at first amorphous, but soon becomes crystalline in the form of calc-spar; when, however, the lime water is hot, crystals of the aragonite form are deposited.

Preparation.—The official salt is prepared by adding a hot solution of sodium carbonate to one of calcium chloride:

$$\underset{\substack{\text{Sodium}\\\text{Carbonate.}}}{Na_2CO_3} + \underset{\substack{\text{Calcium}\\\text{Chloride.}}}{CaCl_2} = \underset{\substack{\text{Calcium}\\\text{Carbonate.}}}{CaCO_3} + \underset{\substack{\text{Sodium}\\\text{Chloride.}}}{2NaCl}$$

The product is a fine, white powder, without odor or taste, and permanent in the air. It is almost entirely insoluble in water, 1 liter dissolving about 18 milligrammes. In the presence of ammonium hydrate or carbonate it is less soluble, but with the other ammonium salts its solubility is increased. Carbon dioxide also increases its solubility: a liter of water saturated with this gas will dissolve 70 milligrammes of the salt. This solubility is increased under pressure up to 3 grammes per liter, but not beyond this point. Such a solution when allowed to stand at ordinary temperatures deposits crystals having the composition $CaCO_3.5H_2O$.

Dilute acetic, hydrochloric, or nitric acid dissolves calcium carbonate with effervescence, leaving no residue.

On heating calcium carbonate to redness with access of air it parts with its carbon dioxide, leaving a residue of calcium oxide.

Creta Præparata, U.S.P., *Prepared Chalk*, is an amorphous calcium carbonate prepared by the elutriation of chalk. The Pharmacopœia of 1870 gave a process for its preparation as follows:

> "Take of Chalk, *a convenient quantity*. Add a little water to the Chalk and rub it into fine powder. Throw this into a large vessel nearly full of water, stir briskly, and, after a short interval, decant the supernatant liquor, while yet turbid, into another vessel. Treat the coarser particles of the Chalk, remaining in the first vessel, in a similar manner, and add the turbid liquid to that previously decanted. Lastly, set the liquor by, that the powder may subside, and, having poured off the water, dry the powder."

Prepared chalk is "a white, amorphous powder, often moulded into conical drops, odorless and tasteless; permanent in the air." In other characters it is practically identical with the precipitated compound.

Uses.—Both of the above preparations are used in medicine; the prepared chalk is preferred by some of the manufacturers of tooth powders on account of its non-crystalline character.

Whiting and *Paris White* are commercial varieties of prepared chalk, not so carefully washed, and therefore not so white. They are used for polishing and for many other purposes where chalk is required in the arts.

STRONTIUM.

Symbol, Sr. *Atomic Weight*, 87.3. *Valence*, II.

History.—The mineral in which strontium was first detected was known as strontianite from its occurrence near the village of Strontian in Scotland; and the metal takes its name from that source. The fact that this mineral contained a peculiar earth was first pointed out by Crawford in 1790. This was confirmed by Hope in 1792, and independently by Klaproth a year later. Davy in 1808 separated the metal in a pure state by electrolysis.

Occurrence.—Strontium is found in nature in the same combinations which characterize barium and calcium,—namely, as carbonate, $SrCO_3$, or strontianite, and as sulphate, $SrSO_4$, or celestine. Many calcium minerals also contain small quantities of strontium. Smaller amounts are found in sea water, in mineral waters, and in certain salt springs. It has also been found in the ashes of some sea plants, as *Fucus vesiculosus*.

Preparation.—Strontium is readily prepared by the electrolysis of the fused chloride, or by repeatedly heating a saturated solution of the fused chloride with an amalgam of 1 part sodium and 4 parts mercury to 90°. There results an amalgam of strontium, which by drying between folds of filter paper and heating in a current of hydrogen yields the pure metal.

Properties.—Metallic strontium is yellow, ductile, and somewhat harder than calcium and lead. It has a specific gravity of 2.5. At a low red heat it melts, and if while hot it is exposed to the air it burns brilliantly. When placed in water it decomposes it with some violence. The salts of strontium have great similarity to those of barium. They impart a red color to flame, and were formerly reputed to be poisonous, but this has been found not to be the case.

STRONTIUM AND THE HALOGENS.

Strontium Chloride, $SrCl_2.6H_2O$.—The readiest method of preparing this salt is by saturating hydrochloric acid with the native carbonate and digesting the solution for some time with excess of carbonate, by which metals like aluminum, iron, and manganese are removed. The hot, concentrated solution deposits, on cooling, acicular crystals of the hexagonal system.

These crystals have a sharp, bitterish taste, and deliquesce on exposure to the air. They are soluble in 1.8 parts of water at ordinary temperatures, and in 0.9 part of boiling water; soluble in alcohol.

On the application of heat the salt loses its water of crystallization at 100°, and at 829° it melts. The anhydrous salt is said to be insoluble in absolute alcohol.

Strontium Bromide, $SrBr_2.6H_2O$. **Strontii Bromidum, U. S. P.**—On saturating hydrobromic acid with strontium carbonate the bromide results, as follows:

$$SrCO_3 + 2HBr = SrBr_2 + H_2O + CO_2.$$

If the native carbonate be used as in the preparation of the chloride, then the solution should be digested for some time with a slight excess of the carbonate, in order to remove other bases. The clear solution is concentrated and allowed to crystallize.

Properties.—Strontium bromide occurs in transparent, colorless crystals, odorless, and having a bitter, saline taste, and an alkaline reaction. It is a very deliquescent salt; dissolves in 1.05 parts of water at 15°, and in 0.5 part of boiling water. "It is readily soluble in alcohol, and is precipitated from this solution upon the addition of an equal volume of ether, in which it is insoluble."

On the application of heat the crystals melt in their water of crystallization, and then lose all their water, amounting to 30.4 per cent. The anhydrous salt fuses at 630°.

Strontium Iodide, $SrI_2.6H_2O$. **Strontii Iodidum, U. S. P.**—When hydriodic acid is saturated with strontium carbonate the iodide results, as follows:

$$SrCO_3 + 2HI = SrI_2 + H_2O + CO_2.$$

The solution is filtered, concentrated to a small bulk, and set aside to crystallize. Strontium iodide may also be prepared by saturating a solution of strontium hydrate with iodine in the same manner as in the preparation of potassium iodide. As the result is strontium iodide and iodate, and the latter has to be converted into the former by ignition, it is doubtful if this process is any more economical than the one first given.

Properties.—Strontium iodide is officially described as occurring in "colorless, transparent, hexagonal plates, odorless, and having a bitterish, saline taste. Deliquescent, and colored yellow by exposure to air and light," on which account it is directed to be kept in "dark amber-colored, glass-stoppered vials." The salt is soluble in 0.6 part of water at 15°, and in 0.27 part of boiling water. It is soluble in alcohol, and slightly in ether.

On the application of a gentle heat, the crystals melt in their water of crystallization, and at a higher temperature lose all of their water, amounting to 24.05 per cent. When the temperature approaches redness, the salt is decomposed with loss of iodine, strontium oxide remaining. The aqueous solution is neutral, or very slightly acid, to litmus paper.

STRONTIUM AND OXYGEN.

Strontium Monoxide, SrO.—This compound of strontium may be prepared in small quantity by heating the nitrate, but on a large scale it is obtained by heating the carbonate in large kilns similar to those used in preparing lime.

Properties.—When prepared by heating the nitrate, this compound forms in grayish-white, porous, infusible masses. That made by heating the carbonate is found in the form of powder or pressed into bricks. The latter form is that in which it is best adapted for use in the sugar industry. It is employed to dissolve in water, forming the hydrate, for use in the recovery of certain varieties of sugar.

Strontium Dioxide, SrO_2, is formed when the hydrate is mixed with hydrogen dioxide. It occurs in pearly scales, having the formula $SrO_2.8H_2O$. When these crystals are heated they lose water, leaving the dioxide as a light, white powder, in an anhydrous condition, which does not melt at a red heat, but gradually loses oxygen.

Strontium Hydrate, $Sr(OH)_2$, is usually obtained by dissolving the monoxide in water, but it may be prepared in small quantity by precipitation of a solution of strontium nitrate with sodium hydrate. This hydrate is moderately soluble in hot water, and when the hot solution cools, crystals are deposited having the formula $Sr(OH)_2.8H_2O$. The crystals dissolve in 50 parts of cold water and in 2.4 parts of boiling water. On the application of heat the water of crystallization is driven off, and at a higher temperature the hydrate is reconverted into oxide.

OXYGEN SALTS OF STRONTIUM.

Strontium Sulphate, $SrSO_4$, occurs in nature as celestine, in transparent rhombic prisms or in fibrous masses, having the specific gravity 3.89. Celestine usually has a light-bluish shade of color, from which it takes its name. The sulphate may be prepared by adding sodium sulphate to a soluble salt of strontium, as the nitrate. It is soluble in 6895 parts of cold water, and in 9638 parts of boiling water. The salt is quite easily decomposed by boiling it with solution of potassium or sodium carbonate. It fuses when strongly heated.

Strontium Nitrate, $Sr(NO_3)_2$.—This salt is prepared by dissolving strontium carbonate in dilute nitric acid. As ordinarily obtained it separates in anhydrous octohedrons; these are permanent in the air. When a hot, dilute solution of strontium nitrate is allowed to cool slowly, monoclinic prisms or plates separate with 4 molecules of water of crystallization; these crystals readily effloresce on exposure to the air.

The anhydrous salt is easily soluble in water, both hot and cold, but scarcely soluble in alcohol.

On the application of heat the salt melts, and at a red heat is decomposed, a residue of strontium oxide remaining.

The principal use of strontium nitrate is in pyrotechnics. Nearly all red fires contain this salt. The following formula will furnish a good red fire: Strontium nitrate, 50 parts; potassium chlorate, 25 parts; pulverized shellac or sugar, 25 parts; powder separately, and carefully mix without friction. An intimate mixture is best made by passing the powders through a sieve.

Strontium Carbonate, $SrCO_3$, occurs native as strontianite in the form of rhombic prisms. It is prepared by precipitating a soluble salt of strontium with sodium carbonate. The salt is soluble in 18,045 parts of cold water. On gentle ignition it is decomposed, yielding a residue of strontium oxide; this decomposition takes place more readily than in the case of either the barium or calcium carbonate. It may be decomposed by boiling with a solution of ammonium chloride.

The chief use of strontium carbonate is for the purpose of readily furnishing the other strontium salts. It is constantly formed and again converted into oxide in the recovery of sugar from certain varieties of molasses.

Such salts of strontium as have not been described in the preceding pages may be prepared by processes similar to the corresponding barium or calcium salts.

BARIUM.

Symbol, Ba. *Atomic Weight*, 136.9. *Valence*, II.

History.—The metal barium was first prepared by Davy in 1808, although its compounds were previously well known, and had received the name of baryta.

Occurrence.—Barium sulphate as heavy spar, and barium carbonate as witherite, are the chief natural forms of this metal. More rarely it is found in barytocelestite $(BaSrCa)SO_4$, barytocalcite $(BaCa)CO_3$, and in many ores of manganese, as psilomelane, $(MnBa)O + MnO_2$. A number of silicates contain small quantities of barium, and it is found in some mineral waters. Barium is, further, found in sea water, in sea plants, and in the ash of certain woods, notably that of the beech.

Preparation.—Davy prepared barium by electrolysis of the chloride in the presence of mercury, the resulting amalgam was heated in a tube containing petroleum, whereby the metallic barium was left behind as a white powder. Bunsen succeeded in preparing it by electrolyzing a thick mixture of very dilute hydrochloric acid and barium chloride at a temperature of 100° in the presence of mercury. This resulted in a crystalline barium amalgam, which, on heating, left the barium as a tarnished, porous mass.

Properties.—Barium is a yellowish-white metal, which melts at a red heat. It is not volatile under ordinary circumstances.

When exposed to the air it readily oxidizes, and if sufficiently heated takes fire. Its specific weight is about 3.75. When thrown on water, it decomposes it at ordinary temperatures like sodium.

BARIUM AND THE HALOGENS.

Barium Chloride, $BaCl_2.2H_2O$.—The easiest method of preparing this salt is by dissolving native barium carbonate, witherite, in dilute hydrochloric acid. The resulting solution contains, in addition to barium, the chlorides of calcium, iron, manganese, etc. ; these are removed by allowing the solution to remain for some time in contact with an excess of the carbonate, whereby the impurities are precipitated. The clear filtered solution is then neutralized exactly with hydrochloric acid, and evaporated to crystallize.

Commercially, the chloride of barium is prepared by fusing finely-powdered heavy spar with charcoal :

$$BaSO_4 + 4C = BaS + 4CO.$$
$$BaS + 2HCl = BaCl_2 + H_2S.$$

Properties.—Barium chloride occurs in colorless, glistening, rhombic tables, permanent in the air, having a disagreeable, bitterish, saline taste, and a neutral reaction. Like all the other compounds of barium, this salt is heavy, having a specific gravity of 3.05. It is soluble in 2.5 parts of water at 15°, and in about 1.5 parts of boiling water. It is insoluble in concentrated hydrochloric acid and in absolute alcohol. At ordinary temperatures over sulphuric acid the salt loses one molecule of water of crystallization, at 120° it becomes anhydrous, and at a red heat it melts. When it is melted with free access of air it loses chlorine, or, below the melting point, in presence of steam, it gives off some hydrochloric acid, the residue reacting alkaline.

The anhydrous salt on exposure to the air takes up two molecules of water.

Barium chloride is an active poison, although in small doses it has been used some in medicine.

Uses.—The chief uses of barium chloride are as a reagent for the detection and estimation of sulphuric acid, and as a preventive against boiler incrustation.

Barium Bromide, $BaBr_2.2H_2O$, and *Barium Iodide*, $BaI_2.2H_2O$, are known and have been prepared, but appear to have no especial value or use.

BARIUM AND OXYGEN.

Barium Monoxide, BaO, may be obtained by burning the metal in the air; but it is prepared by heating the nitrate in an iron crucible until there is no further evolution of red fumes.

This compound usually occurs as a grayish-white, porous mass, which has a specific gravity of 5.72, and melts at a white heat.

In contact with water it slakes with considerable evolution of heat, forming barium hydrate, $Ba(OH)_2$.

Barium monoxide is used in the manufacture of oxygen by the Brin process.

Barium Dioxide, BaO_2. **Barii Dioxidum, U. S. P.,** *Barium Peroxide.*—This compound is prepared by heating the monoxide in a stream of dry air or oxygen, which is best accomplished at a temperature of about 450°.

Properties.—Barium dioxide occurs as "a heavy, grayish-white, or pale yellowish-white, amorphous, coarse powder, odorless and tasteless. When exposed to the air it slowly attracts moisture and carbon dioxide, and is gradually decomposed. Almost insoluble in cold water, with which, however, it forms a definite hydrate, and to which it imparts a decidedly alkaline reaction."

When heated to bright redness it fuses, and loses one atom of oxygen. Hydrochloric and the other mineral acids decompose it with the formation in the cold of hydrogen dioxide and a barium salt:

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2.$$

Barium dioxide is directed by the Pharmacopœia to be kept in well-closed vessels, and is used for the preparation of the official hydrogen dioxide.

Barium Hydrate, $Ba(OH)_2$.—When barium monoxide is treated with water, the hydrate is formed according to the following reaction:

$$BaO + H_2O = Ba(OH)_2.$$

If just enough water is added to form the compound, the result is a white powder, which at a low red heat melts to an oily liquid, which solidifies on cooling to a crystalline mass. In this condition it has a specific gravity of 4.495, and when dissolved in water forms crystals having the formula $Ba(OH)_2.8H_2O$. These crystals, on exposure to the air, fall to a white powder with a loss of seven molecules of water. On a commercial scale, barium hydrate is prepared by heating the carbonate in a current of steam:

$$BaCO_3 + H_2O = Ba(OH)_2 + CO_2.$$

The resulting mass is dissolved in water, allowed to settle, and the clear solution decanted and crystallized.

It is soluble in 20 parts of water at ordinary temperatures, and in 3 parts of boiling water, forming a strongly alkaline solution, which is extensively used as a reagent under the name of baryta water.

OXYGEN SALTS OF BARIUM AND THE HALOGENS.

Barium Chlorate, $Ba(ClO_3)_2$, is prepared by saturating aqueous chloric acid with barium carbonate. It crystallizes in monoclinic prisms, and is easily soluble in water.

Barium Iodate, $Ba(IO_3)_2$, is obtained by double decomposition between potassium iodate and barium chloride; barium iodate separates out, since it requires about 3000 parts of water to dissolve it; it is soluble in 600 parts of boiling water. Its chief use is for the preparation of iodic acid.

BARIUM AND SULPHUR.

Barium Monosulphide, BaS, is formed when hydrogen sulphide is passed over heated baryta, as long as water is formed. For the production of larger quantities, an intimate mixture of 100 parts barium sulphate, 25 parts of coal, and 20 parts of common salt is made into a plastic mass with water, dried, and heated for several hours to whiteness.

Properties.—Barium monosulphide is a reddish-white or, from the presence of coal, a grayish-white mass, which in the presence of water is decomposed into barium hydrate and barium sulphydrate, which are dissolved. When a mixture of 5 parts of the barium monosulphide and 1 part of sulphur is boiled with water and allowed to evaporate in a vacuum, colorless crystals separate, having the formula $BaS.6H_2O$.

By using larger proportions of sulphur several compounds containing more of this element may be obtained; of these the following are known: *barium trisulphide*, BaS_3, *barium tetrasulphide*, $BaS_4.H_2O$, and *barium pentasulphide*, BaS_5.

Barium Sulphydrate, $Ba(SH)_2$, is prepared by passing hydrogen sulphide into a solution of barium hydrate until saturated; by evaporating in a vacuum it crystallizes in white, four-sided prisms.

OXYGEN SALTS OF BARIUM.

Barium Sulphate, $BaSO_4$, *Heavy Spar*.—This is the most abundant native compound of barium, and on that account it furnishes the starting-point in the preparation of the other barium compounds. It is often found in irregular masses, but also comes in well-formed rhombic prisms or tables.

Barium sulphate is prepared by precipitating any soluble barium salt with dilute sulphuric acid. That made in this manner is extensively used as a pigment in water-colors under the name of *blanc fixe* or *permanent white.*

Properties.—The precipitated salt is a heavy, fine, white powder. It has a specific gravity of 4.53, while that of the native mineral, according to H. Rose, is 4.486. It is almost absolutely insoluble in water, since 1 part requires 400,000 parts of water to dissolve it. In the freshly precipitated state it is soluble in concentrated sulphuric acid, but it is thrown down on dilution with water.

Barium sulphate is decomposed by fusing with three to four times its weight of sodium carbonate, by which barium carbonate and sodium sulphate result; the latter can be removed by solution in water.

In order to precipitate barium sulphate in an impalpable powder, the solution of barium chloride, having a specific gravity of 1.19, is treated in the cold with dilute sulphuric acid having a specific gravity of 1.245; the resulting precipitate is collected, washed with cold water, and sent into commerce in the moist state. This compound is not only used as an unalterable paint, but also for giving weight to cards and paper. The finely-powdered mineral is employed to mix with lead carbonate in the manufacture of the cheaper paints, but, on account of its crystalline character, it has not the covering power of the pure lead compound or of the precipitated barium sulphate.

Barium Disulphate, BaS_2O_7, is prepared by adding finely-powdered barium sulphate to fuming sulphuric acid until it forms a syrupy solution. On heating this to 150° the disulphate deposits in glistening, granular crystals.

Barium Dithionate, $BaS_2O_6.2H_2O$, is prepared by decomposing manganese dithionate with barium sulphide. Its solution on evaporation deposits glittering rhombic crystals. It is soluble in 4 parts of water at ordinary temperatures, and in 1.1 parts of boiling water. Heat converts it into barium sulphate without change of form.

Barium Nitrate, $Ba(NO_3)_2$.—Nitric acid is saturated with barium carbonate or sulphide in order to obtain this salt. As thus prepared it forms permanent, colorless, anhydrous, octohedral crystals. It is soluble in 12 parts of water at ordinary temperatures, and in 3 parts of boiling water; insoluble in alcohol.

Barium nitrate is used as a reagent, but the greatest consumption of it is to furnish the green to colored fires. The following formula will produce a satisfactory color: Potassium chlorate, 50 parts; barium nitrate, 25 parts; sugar or shellac, 25 parts. Each ingredient to be pulverized separately, and then all carefully mixed and run through a sieve. Sulphur is a frequent constituent of colored fires, and may be used in place of the sugar or shellac, but it renders the fires more liable to inflame spontaneously.

Barium Carbonate, $BaCO_3$.—This compound occurs native as witherite, or it may be prepared by adding sodium carbonate to a soluble salt of barium. The native salt occurs in glistening, rhombic crystals, but the precipitated compound is a white powder. It is soluble in 14,000 parts of cold water, and in 15,400 parts at 100°.

When heated to redness barium carbonate loses no carbon dioxide, but in the flame of the oxyhydrogen lamp it melts and gives off this gas slowly. The decomposition takes place more readily and at a lower temperature in the presence of carbon or when steam is passed over it.

Barium carbonate is used considerably as a starting-point for other compounds, and in chemical analysis. On account of its poisonous properties the carbonate has had considerable use as a rat poison.

CHAPTER III.

THE MAGNESIUM GROUP.

MAGNESIUM.

Symbol, Mg. *Atomic Weight*, 24.3. *Valence*, II.

History.—Attention was first directed to the magnesium salts about the close of the seventeenth century by Grew, a physician of London. He found a peculiar salt in the mineral spring at Epsom, which salt soon became celebrated for its medicinal virtues. The metal was first isolated by Davy, in 1808, although he did not obtain it in a pure condition. Bussy was the first to obtain a distinct quantity of the metal, which he accomplished by acting on the fused chloride with potassium. Bunsen, in 1852, prepared it by electrolysis of the chloride, and Sainte-Claire-Deville and Caron, in 1857, devised a process for its production on a commercial scale. The compounds of magnesium and manganese were not distinguished from each other for a long time, and much confusion regarding them was the result. The distinction was first clearly pointed out by Black, in 1755. Later, magnesium came to be known as the metal existing in *magnesia alba*, and manganese as that in *pyrolusite* (manganese dioxide), then called *magnesia nigra*.

Occurrence.—The metal is not found in the uncombined state in nature. Its compounds, however, are almost as widely distributed as those of calcium, although not in such large quantities. The principal minerals containing it are magnesite, $MgCO_3$; dolomite, $(MgCa)CO_3$; kieserite, $MgSO_4.H_2O$; carnallite, a chloride of magnesium and potassium, $KCl,MgCl_2.6H_2O$; and the following silicates: talc, asbestos, meerschaum, enstatite, and serpentine. Magnesium salts are found in plants, in which they may to a certain extent replace the salts of calcium. As phosphate magnesium is found in the bones and urine of animals.

Preparation.—Magnesium is now usually prepared by the electrolysis of the fused chloride. The decomposition is facilitated by the presence of potassium chloride, so that the mineral carnallite becomes a chief source for it. The precaution must be taken to have no kieserite present, since it is liable to give rise to violent explosions. The electric current employed is furnished by a powerful dynamo. Magnesium is liberated at the negative pole. The vessel in which the decomposition is effected is made of especially prepared cast-steel, which acts as the negative pole; the positive pole is made of gas-carbon. In order to prevent the oxidation of the metal, a stream of hydrogen or nitrogen is led through the vessel during the operation.

The metal is also prepared to some extent by throwing into a red-hot crucible 6 parts of anhydrous magnesium chloride, 1 part of fluor-spar, 1 part of sodium and potassium chloride (obtained by fusing together 7 parts of sodium chloride and 9 parts of potassium chloride), and 1 part of finely-cut sodium. A violent reaction ensues, and when this has ended the covered crucible is removed from the fire, and the contents stirred with an iron rod to cause the small particles of magnesium to unite. When cold the metal is removed and washed with water.

The product from both of the preceding processes is quite impure, containing carbon, silicon, and nitrogen. It is purified by distillation from an iron vessel at about 1000°. A stream of hydrogen or coal-gas is passed through the crucible in order to prevent oxidation. The purified metal is pressed into wire by peculiar machinery, and then rolled into ribbon.

Properties.—Magnesium is a silver-white, strongly lustrous metal, having a specific gravity of 1.75. It is unchangeable in dry air, but in the presence of moisture it gradually becomes covered with a film of oxide. When heated without access of air, magnesium melts at about 500° and boils at 1000°. Heated in the air it ignites, and burns with a blinding white light which is especially rich in actinic rays. Water is not decomposed by magnesium at ordinary temperatures, but at 100° decomposition takes place, with evolution of hydrogen and the formation of magnesium oxide.

Uses.—On account of the chemical activity of the magnesium light it is useful in photography, and enters into the composition of the numerous "flash-light" powders. Previous to the development of electric lighting it was used in making strong lights for signalling purposes. It is used in pyrotechny. The celebrated Bengal fires are made as follows: Red—1 part of pulverized shellac, 5 parts of dried strontium nitrate, 2.5 parts of powdered magnesium. Green—1 part of pulverized shellac, 6 parts of dried barium nitrate, 2.5 parts of powdered magnesium.

Magnesium also has some use in the laboratory, where, on account of its freedom from arsenic, it may replace zinc in Marsh's test.

MAGNESIUM AND THE HALOGENS.

Magnesium Chloride, $MgCl_2.6H_2O$. — Sea water and most mineral waters contain magnesium chloride. In the solid state it is found abundantly as carnallite, $KCl, MgCl_2.6H_2O$, at Stassfurt; also in a number of the double salts in that locality. It may be prepared by dissolving magnesite in hydrochloric acid; but, since it is a by-product of not much value in the preparation of potassium chloride from carnallite, it practically all comes from that source.

Properties.—Magnesium chloride occurs in colorless, very deliquescent, monoclinic crystals. It cannot be deprived of its water of crystallization by heat, since, when heated, it decomposes with evolution of hydrochloric acid and formation of magnesium oxychloride.

The anhydrous salt, therefore, is obtained by adding ammonium chloride, evaporating carefully to dryness, and then igniting carefully in a platinum dish to volatilize the ammonium salt; or it may be prepared by drying the crystallized salt in a stream of hydrochloric acid gas.

Anhydrous magnesium chloride occurs in transparent, laminated, pearly plates, which dissolve in water with the evolution of heat. It possesses a bitter, saline taste, and is readily soluble in water. With magnesium oxide it forms an oxychloride which is insoluble in water. If magnesium oxide is added to a 30-per-cent. magnesium chloride solution to a creamy consistence, the mixture solidifies.

Uses.—Magnesium chloride is used in the preparation of artificial stone, and as a finisher of cotton goods in dye-works.

Magnesium Oxychloride.—When an aqueous solution of magnesium chloride of 1.16 to 1.26 specific gravity is mixed with freshly-prepared magnesium oxide, the mass after some time hardens, so as to be capable of taking a high polish. It has a composition represented by the formula $Mg_{11}Cl_2(OH)_{20}.4H_2O$. On exposure to the air for some time it absorbs carbon dioxide. Another oxychloride is formed when magnesium sulphate, containing ammonium hydrate and chloride, is exposed to the air for some time; the crystalline precipitate, which is deposited, has the composition $Mg_3Cl(OH)_5.4H_2O$.

Anhydrous magnesium chloride forms with alcohol a compound in which the latter replaces the water of crystallization. This crystalline compound, therefore, has the formula $MgCl_2.6C_2H_6O$.

Magnesium Bromide, $MgBr_2.6H_2O$, occurs in sea water and in a number of salt springs. It is this salt more than any other that is the source of bromine. It may be prepared by heating magnesium in bromine vapor, but a cheaper method consists in passing bromine vapor over an ignited mixture of magnesium oxide and charcoal.

The anhydrous salt forms in solid, white, crystalline masses, which are very deliquescent, and become hot in contact with water. When the salt contains water of crystallization, it loses hydrobromic acid on the application of heat, leaving a residue of magnesium oxybromide.

Magnesium Iodide, MgI_2, occurs associated with the bromide, or it may be prepared by passing iodine vapor over magnesium. It forms very deliquescent, hydrated crystals, which readily decompose with liberation of iodine.

Magnesium Fluoride, MgF_2, is found in nature as the mineral sellaite. It is insoluble in water. It may be prepared by evaporating magnesium oxide with an excess of aqueous hydrofluoric acid to dryness. It forms amorphous masses, which may be obtained in crystals by fusing with sodium chloride and, after cooling, removing the salt by washing with water.

MAGNESIUM AND OXYGEN.

Magnesium Oxide, MgO. **Magnesia, U. S. P.**—Black, in 1755, appears to have been the first to prepare this oxide. He noted its property of dissolving in sulphuric acid, which served to distinguish it from lime.

Occurrence.—Magnesium oxide is found native in the rare mineral periclase, found at Mount Somma, near Naples. This mineral, however, contains some ferrous oxide.

Preparation.—Magnesia is prepared on a large scale by heating the carbonate. When the light carbonate is ignited, the light or calcined magnesia, *magnesia usta*, results. When a denser carbonate is used, the result is heavy magnesia, **Magnesia Ponderosa, U. S. P.** With the official carbonate the reaction is as follows:

$$(MgCO_3)_4Mg(OH)_2.5H_2O = 5MgO + 6H_2O + 4CO_2.$$

The operation is conducted in iron or earthenware crucibles; at 300° the decomposition readily takes place, and it is known to be complete when a small quantity, taken from the middle of the vessel with an iron spoon and cooled, gives no effervescence with dilute hydrochloric acid.

Probably the most important feature in the successful manufacture of this compound is that of avoiding too high a temperature. In order to prevent parts of the powder from becoming too hot it should be stirred frequently, or it has been recommended to perform the ignition in shallow pans, so that the depth of the carbonate does not exceed 2 to 3 inches. Much also depends upon the purity and physical condition of the carbonate employed.

Properties.—Official magnesia occurs as a loose, white, odorless powder; possessing an earthy but not a saline taste. It is almost insoluble in water (1 to 55,368), insoluble in alcohol, but readily soluble in dilute acids without effervescence.

The presence of ammonium salts materially increases its solubility in water. In moist air it readily absorbs moisture and carbon dioxide, becoming converted into a basic carbonate.

Magnesia is not visibly affected by any temperature below that of the oxyhydrogen flame, but it will, at lower temperatures, become more dense and crystalline. "On stirring 1 part of Magnesia with 15 parts of water, in a beaker, and allowing the mixture to stand for about half an hour, it will form a gelatinous mass of sufficient consistence to prevent it from dropping out when the glass is inverted."—U. S. P. The heavy magnesia is a denser and finer powder, but in most other characters resembles the light compound.

Magnesium Hydrate, $Mg(OH)_2$, occurs in nature as the mineral brucite. It may be prepared by allowing a not overheated magnesium oxide to stand in contact with water, or more quickly by heating the same compound with water to 150°. Sodium or potassium hydrate precipitates magnesium hydrate from solutions of the salts, like the sulphate or chloride.

Magnesium hydrate is a white, nearly insoluble powder. It is easily soluble in solutions of ammonium salts. At 100° magnesium hydrate is not affected, but when the temperature approaches redness, it is easily converted into oxide. It is sufficiently soluble in water to impart an alkaline reaction to the latter.

SALTS OF MAGNESIUM.

Magnesium Sulphite, $MgSO_3.6H_2O$, is prepared by double decomposition between magnesium sulphate and sodium sulphite; or it may be made by adding sulphurous acid in excess to a mixture of 8 parts of magnesium oxide in 16 parts of water.

Properties.—Magnesium sulphite is a white, crystalline powder, becoming oxidized on exposure to air, odorless, having a slightly bitter, somewhat sulphurous taste, and a neutral or slightly alkaline reaction. It is soluble in 20 parts of water at 15°, and in 19 parts of boiling water; insoluble in alcohol. When heated to 200° the salt loses its water of crystallization, amounting to 50.9 per cent., and is converted into magnesia and anhydrous magnesium sulphate.

Magnesium sulphite was official in the U. S. Pharmacopœia, but was dropped from the last revision. It has some use in medicine, as, on account of its sparing solubility, its taste is not quite so disagreeable as the other sulphites. It has the medicinal properties of the sulphites in general.

Magnesium Sulphate, $MgSO_4.7H_2O$. **Magnesii Sulphas, U. S. P.**—Epsom salt became known about the end of the seventeenth century, because of its valuable purgative qualities, and was designated on the Continent of Europe as bitter salt and *Sal Anglicum*.

Occurrence.—Magnesium sulphate occurs in many mineral waters, the most notable being those of Pullna and Seidlitz, in Bohemia, of Epsom, in England, of Friedrichshall, in Germany, and Hunyadi János, in Hungary. Under the name of kieserite magnesium sulphate is found at Stassfurt, having the composition $MgSO_4.H_2O$. The upper layer of this salt deposit, known as *Abraumsalz*, is a mixture of magnesium sulphate with a number of other salts.

Extraction.—Formerly much magnesium sulphate was obtained by the concentration of natural bitter waters and by the evaporation of the mother liquors after the crystallization of sodium chloride from sea-water. At the present time large quantities are made as a by-product in the manufacture of carbon dioxide for use in mineral waters. Magnesite is used to furnish this gas and sulphuric acid is used to effect its liberation, as follows:

$$\begin{array}{ccccccccc} MgCO_3 & + & H_2SO_4 & = & MgSO_4 & + & CO_2 & + & H_2O. \\ \textbf{Magnesite.} & & \textbf{Sulphuric} & & \textbf{Magnesium} & & \textbf{Carbon} & & \textbf{Water.} \\ & & \textbf{Acid.} & & \textbf{Sulphate.} & & \textbf{Dioxide.} & & \end{array}$$

After the escape of carbon dioxide, the residue is dissolved in hot water, neutralized with magnesite, some barium sulphide added, and the mixture allowed to stand for some time in order to separate iron; finally, the clear liquid is concentrated and allowed to crystallize. The *abraumsalz* above mentioned is also employed as a source of magnesium sulphate. This salt is exposed to a damp atmosphere, or suspended in baskets over open evaporators, so that it is brought in contact with the ascending steam; by this means the soluble magnesium and sodium chlorides are dissolved, while the kieserite remains behind. Kieserite is not easily dissolved by water, but on contact with that liquid it disintegrates and is converted into Epsom salt, containing 7 molecules of water; in this form it is dissolved and recrystallized.

Properties.—Magnesium sulphate crystallizes from water in colorless, rhombic prisms, or in small acicular crystals; the latte form is obtained by allowing the crystallization to take plac from hot concentrated solutions. The salt is without odor, an has a cooling, saline, bitter taste; the crystals slowly effloresc in dry air. It is soluble in 1.5 parts of water at 15°, and in 0.7 part of boiling water; insoluble in alcohol. When heated to 52° the salt loses 1 molecule of water, from this temperature up to 132° it loses 5 additional molecules, and at 200° to 238° the remaining molecule is removed and the salt becomes anhydrous. The aqueous solution is neutral to litmus.

With the salts of the alkali metals magnesium sulphate forms double salts, as $MgSO_4.K_2SO_4.6H_2O$; $MgSO_4.(NH_4)_2SO_4.6H_2O$, etc. When anhydrous magnesium sulphate is dissolved in hot concentrated sulphuric acid, six-sided tabular crystals separate out on cooling, which have the composition $MgSO_4.H_2SO_4$.

Uses.—Magnesium sulphate is used in medicine as an active and safe cathartic. It also has some use in dyeing and calico printing as a finisher. When this salt is used with aniline colors, the finished goods are found to better resist the action of soap.

Magnesium Nitrate, $Mg(NO_3)_2.6H_2O$, is prepared by neutralizing nitric acid with magnesium carbonate. It forms deliquescent monoclinic prisms or acicular crystals. From hot solutions it separates with 2 molecules of water of crystallization. The crystals are soluble in 0.5 part of water at 15°, and in 9 parts of alcohol.

Normal Magnesium Phosphate, $Mg_3(PO_4)_2$, is found in bones, in the seeds of many plants, and in a number of minerals. It is precipitated when a solution of trisodium orthophosphate is added to one of magnesium sulphate. One part of the salt requires 5000 parts of water to dissolve it.

Magnesium Hydrogen Phosphate, $MgHPO_4$, is formed when a solution of ordinary sodium phosphate, Na_2HPO_4, is added to one of magnesium sulphate. On standing in contact with water, this precipitate becomes crystalline with 7 molecules of water. One part of this crystalline precipitate is soluble in 322 parts of water.

Ammonium Magnesium Phosphate, $Mg(NH_4)PO_4.6H_2O$.—This salt frequently separates from decomposing urine, and large crystals of it have been found in some varieties of guano. It is formed when ammonium chloride and hydrate are mixed with a solution of magnesium sulphate, and then a solution of a soluble phosphate added. The crystals which are thus produced are transparent, quadratic prisms, soluble in 15,000 parts of water at 15° and in 44,000 parts of ammoniacal water. At 100° five molecules of water are given off without loss of ammonia, and at higher temperatures the remainder of the water and the ammonia escape, leaving magnesium pyrophosphate, $Mg_2P_2O_7$.

Magnesium Arsenate and *Magnesium Ammonium Arsenate* are similar in their method of preparation and properties to the corresponding phosphates.

Magnesium Borate.—When solutions of borax and magnesium sulphate are mixed in the cold, no precipitation takes place, but on long boiling a precipitate forms having the composition $Mg(BO_2)_2,2Mg(OH)_2.7H_2O$. This compound has had some use as an antiseptic.

Magnesium Carbonate, $MgCO_3$.—This is the normal magnesium carbonate, and is found abundantly in nature as magnesite. It is somtimes found in rhombohedral crystals, which are isomorphous with those of calcite. In pharmacy and medicine we are concerned chiefly with the artificially prepared or basic magnesium carbonate $(MgCO_3)_4,Mg(OH)_2.5H_2O$, **Magnesii Carbonas,** U. S. P. This compound became known as a valuable medicinal agent about the beginning of the eighteenth century, under the name of *magnesia alba.*

Preparation.—10 parts of magnesium sulphate and 12 parts of sodium carbonate are each dissolved separately in 80 parts of distilled water, the solutions are mixed in the cold, and the mixture boiled for 15 minutes. The precipitate is collected on a muslin filter and washed with hot water until the washings cease to give a reaction with barium chloride for sulphuric acid. The heavy carbonate of magnesia, *magnesia carbonas ponderosa* of the British Pharmacopœia, is prepared by dissolving each of the above salts in 20 parts of water, mixing, and evaporating the resulting mixture to dryness. The dry residue is then washed thoroughly with hot water until all sodium sulphate is removed. The product is a dense powder. The reaction which takes place in these processes is as follows :

$$\underset{\substack{\text{Magnesium}\\\text{Sulphate.}}}{5MgSO_4} + \underset{\substack{\text{Sodium}\\\text{Carbonate.}}}{5Na_2CO_3} + \underset{\text{Water.}}{6H_2O} = \underset{\text{Official Magnesium Carbonate.}}{(MgCO_3)_4,Mg(OH)_2.5H_2O} +$$

$$\underset{\substack{\text{Sodium}\\\text{Sulphate.}}}{5Na_2SO_4} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{CO_2}.$$

The method of Pattinson consists in igniting dolomite, a magnesium and calcium carbonate, and treating the product with solution of carbon dioxide under a pressure of 5 to 6 atmospheres. The magnesium carbonate goes into solution much easier than the calcium carbonate. The clear solution is separated from the precipitate of the latter, and on heating deposits a precipitate of the official carbonate, with evolution of some carbon dioxide, which may be used again.

Properties.—The official magnesium carbonate comes in commerce in loose, white, easily-pulverized masses, which are readily reduced to a fine, white, amorphous powder, without odor, having an earthy taste, and permanent in the air. It dissolves in 2500 parts of cold water, and in 9000 parts of hot water, and imparts to the water an alkaline reaction ; alcohol exerts no solvent action upon it. Dilute acids dissolve it with active effervescence, and without leaving any residue.

Solution of ammonium salts have considerable solvent action on magnesium carbonate, and in the presence of ammonium chloride no precipitation of the carbonate will occur.

On the application of heat, water is first given off, and at 170° (Mendelejeff) the decomposition of the carbonate is complete, magnesium oxide remaining. This is considerably lower than the temperature of dissociation given by other authorities, and would consequently require more time than that usually given for the preparation of magnesium oxide.

When the official magnesium carbonate is shaken with water until a uniform mixture results, and carbon dioxide is passed in, there results a clear solution of *acid magnesium carbonate*, $MgH_2(CO_3)_2$, which has not been separated in the solid state. This solution on exposure to the air, and warming to 50°, deposits crystals of the neutral carbonate with 3 molecules of water, $MgCO_3.3H_2O$, or at a winter temperature $MgCO_3.5H_2O$ separates. Under ordinary atmospheric pressure 1 part of magnesium carbonate requires 761 parts of carbonic acid water to dissolve it, under 3 atmospheres of pressure the solubility is 1 to 134, and at 6 atmospheres it is 1 to 76 of the carbonic acid water.

The *Liquor Magnesii Carbonatis* of the British Pharmacopœia is such a solution, and contains about 2 per cent. of the official carbonate. It is clear, and free from bitter taste.

Uses.—Magnesium carbonate is used in medicine as an antacid, and in the presence of acids becomes cathartic in its action.

Magnesium Silicates.—A number of these compounds occur widely distributed in the mineral kingdom. Talc has the composition $3MgSiO_3.H_2SiO_3$, serpentine $3MgO,2SiO_2.2H_2O$, etc.

BERYLLIUM (Glucinum, Gl).

Symbol, Be. *Atomic Weight*, 9.03. *Valence*, II.

Historical.—The mineral beryl was formerly supposed to be a compound of silica with calcium or aluminum, but Vauquelin, in 1798, showed the base to be different from both of these, and the name glucina was given to this new earth. Wöhler, in 1828, first obtained the metal, by fusing the chloride with potassium.

Occurrence.—Beryllium occurs in nature in a few rare minerals. Beryl is a silicate of beryllium and aluminum, $3BeSiO_3,Al_2(SiO_3)_3$, which occurs in beautiful hexagonal crystals of a green color; the transparent, green-colored varieties are known as emerald, and those of a bluish-green tint are termed aquamarine. Phenacite is a beryllium silicate of the composition Be_2SiO_4, and chrysoberyl is a beryllium and aluminum oxide, BeO,Al_2O_3.

Preparation.—Metallic beryllium is prepared by passing the vapor of beryllium chloride, along with hydrogen, over heated sodium. A violent reaction occurs, and the chloride is reduced to the metallic state and is obtained in the form of powder. It is afterwards caused to cohere by fusing in a crucible under a layer of sodium chloride. Any of the modern processes for the preparation of aluminum may be successfully applied to the preparation of beryllium.

Properties.—Beryllium is a silver-white, lustrous metal; malleable, and having the specific gravity 1.64. It remains unchanged in the air at ordinary temperatures, but when heated it becomes coated with a thin film of oxide which prevents further change. If the metal be in a finely-powdered state it will inflame when heated in the air. It does not act upon water, even when the latter is boiled with it. Dilute acids, like hydrochloric and sulphuric, dissolve it, as do also the hydrates of sodium and potassium, but nitric acid, even when hot and concentrated, acts on it very slowly.

Beryllium Chloride, $BeCl_2$, is obtained in the anhydrous condition by passing chlorine over a heated mixture of beryllium oxide and charcoal. It is easily fusible and volatile, and may be obtained with 4 molecules of water of crystallization from aqueous solution. The chloride may also be obtained by dissolving the oxide in hydrochloric acid. In many of its characters it resembles magnesium chloride.

Beryllium Bromide, $BeBr_2$, *Iodide*, BeI_2, and *Fluoride*, BeF_2, are known, and may be prepared like the chloride.

Beryllium Oxide, BeO, yields with acids salts having a sweet taste. The solutions of these salts give precipitates of the *hydrate*, $Be(OH)_2$, on the addition of sodium or potassium hydrate; this hydrate is distinguished from that of magnesium by being soluble in excess of the reagent, and from the hydrate of aluminum by its solubility in excess of alkali carbonate.

Beryllium Sulphate, $BeSO_4.4H_2O$, separates from hot, concentrated solutions, while from acid solution $BeSO_4.7H_2O$ crystallizes; it is isomorphous with magnesium sulphate.

Beryllium Nitrate, $Be(NO_3)_2.3H_2O$, is an extremely deliquescent salt, easily soluble in alcohol.

Beryllium Phosphate, $BeHPO_4.3H_2O$, is obtained by precipitating a soluble salt of beryllium with sodium phosphate.

Beryllium Carbonate, $BeCO_3.4H_2O$, separates in crystals of this composition, when a solution of the basic carbonate in carbon dioxide is concentrated over sulphuric acid with exclusion of oxygen.

ZINC.

Symbol, Zn. *Atomic Weight*, 65.10. *Valence*, II.

History.—Paracelsus in the sixteenth century first recognized zinc as a metal. It was known, however, long before that time that certain ores of zinc known as *cadmia* would, when smelted with copper ores, furnish a yellow metal (brass). Works for the preparation of metallic zinc were first established in the year 1743, at Bristol, England.

Occurrence.—It is doubtful if zinc occurs in nature in the metallic state, although it is said to have been found in Australia. The most abundant ore of zinc is the sulphide, or zinc blende, and next the silicate, or calamine, although the carbonate (smithsonite) is often included under the same general term. The most noted European localities are Belgium, Silesia, Saxony, and England. In the United States fully half the zinc is produced in Missouri, although there are important deposits in Pennsylvania, New Jersey, Virginia, Wisconsin, Kansas, and Arkansas.

In the United States there are two ores that are peculiar to the localities named and are not found abroad,—namely, the native oxide, called red oxide, or zincite, and a mixture of zinc oxide with manganese and iron oxide, known as franklinite. Both of these minerals occur at Franklin and Mine Hill, New Jersey.

Zinc has been found in the ashes of some plants which grow in localities where the soil contains the metal.

Preparation.—Zinc ores are first roasted to remove carbon dioxide and water in the case of calamine, and in the blende to convert the sulphide into oxide. The roasted ore is then reduced with charcoal.

Originally the English process was exclusively employed. This consisted in mixing the roasted ore with half its weight of charcoal, and heating in crucibles which were constructed with a tube extending from the bottom of the crucible down to a vessel underneath. This tube was plugged at its opening into the crucible with a piece of wood which was converted early in the operation into porous charcoal, and thus allowed the passage of the zinc vapor down to the receiver below. The top of the crucible was tightly covered. The English process has now given way to the Belgian and the Silesian processes.

The Belgian process is illustrated in the figures as follows: Fig. 68 shows a side view of the retorts placed in the furnace, and Fig. 69 gives a back view of these retorts, showing how the fire reaches them.

FIG. 68.

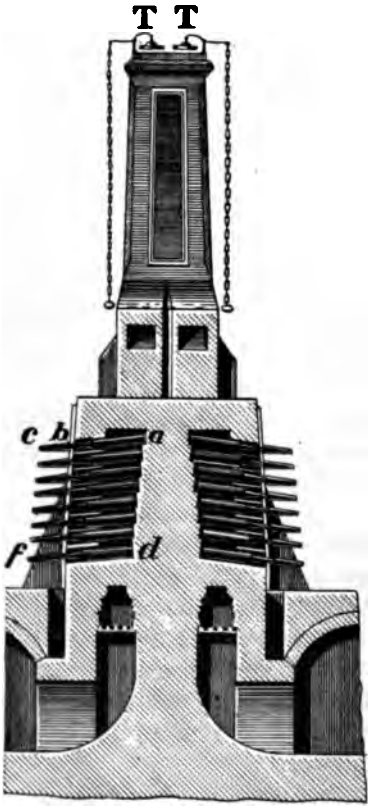
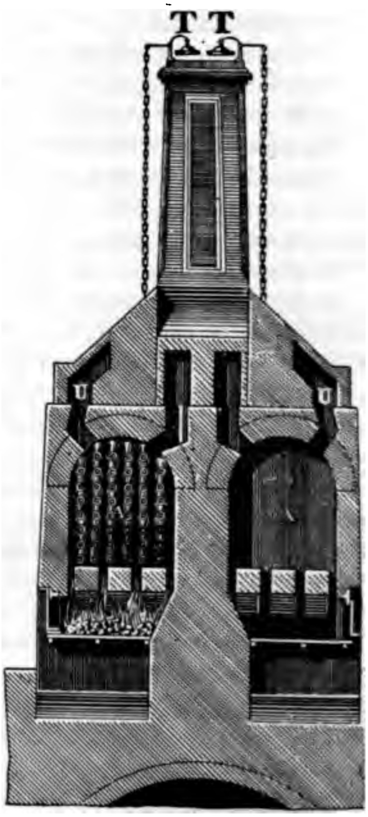


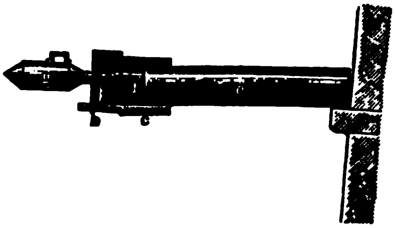
FIG. 69.



Zinc smelting (Belgian process).

The retorts *e*, Fig. 70, are made of fire-clay, and filled with a mixture of powdered coal and roasted ore. They are about 1 meter in length, with an internal diameter of 0.2 meter. To the open end a conical earthenware tube 0.24 meter in length is luted, and to it the condenser, *g*, is fitted; this condenser has a small opening in its end to permit the escape of gases. The charge consists of about 40 pounds of a mixture of 2 parts of roasted ore and 1 part of coal. About 48 of the crucibles are placed in one of the furnaces. On the application of heat carbon monoxide first escapes, and burns at the mouth of the tube (*f*, Fig. 70) with a blue flame. As the metal begins to volatilize the flame becomes much whiter in color; the receiver *g* is then placed in position, and there is condensed in it a mixture of finely-divided metal and oxide ; this is removed after a time, and the metal collected both in the receiver and in the earthenware tube.

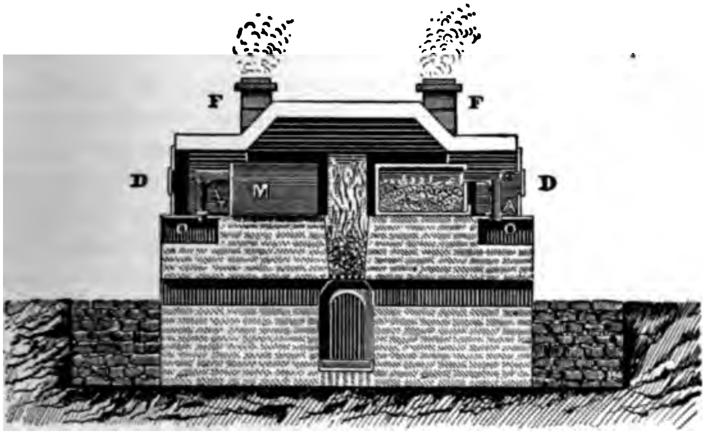
FIG. 70.



Retort of Belgian process.

In the Silesian process is used a retort or muffle of a shape different from that employed in the Belgian method, and it is considerably larger in size. Figs. 71 and 72 show these muffles in position in the furnace, while an enlarged view of a muffle is shown in Fig. 73.

FIG. 71.

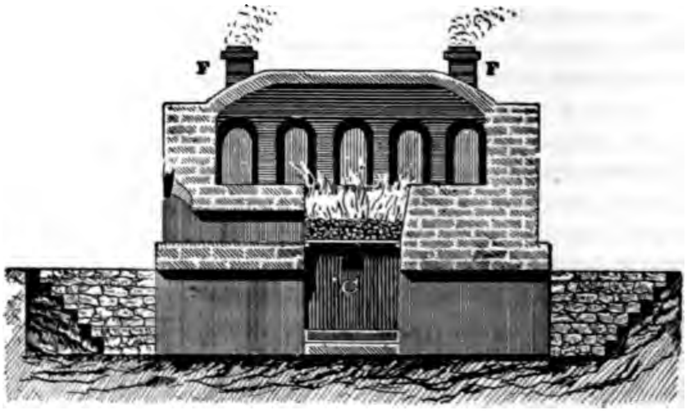


Zinc smelting (Silesian process).

In this process considerably more of the zinc is converted into oxide. A few furnaces are constructed to use the Silesian muffles below and the Belgian retorts above. Gas is sometimes used for fuel.

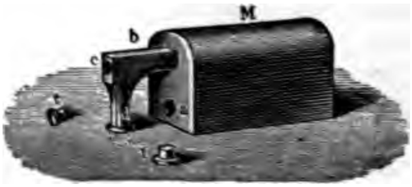
Commercial zinc often contains as impurities lead, carbon, iron, arsenic, and some other metals. It, therefore, requires further purification. This is accomplished by submitting it to distillation in retorts similar to those used in the English method of reduction; that is, with an exit-pipe cemented into the bottom of the vessel. The vapors pass down through this tube and are collected in a vessel beneath. Zinc purified in this manner is usually remelted and cast into rods, rolled into thin sheets, or granulated by pouring into cold water, in which form it is known as "mossy" zinc.

FIG. 72.



Zinc smelting (Silesian process).

FIG. 73.



Crucible of Silesian process.

The Belgian process is chiefly used in the United States, where the output for 1893 amounted to 76,255 tons, valued at $6,214,782. This was about one-fourth of the total production of the world.

Properties.—Zinc is a bluish-white metal, with a lustre which is almost insignificant when compared with that of some other metals. When cast it exhibits a tabular structure. Its specific gravity ranges from 6.9, when it is cast, to 7.2, when it is rolled. It is very ductile, considering its hardness. Its malleability is considerable when pure, but in the impure condition it is quite brittle.

When heated to 100° and not above 150°, its malleability and ductility are materially increased; above 200° it becomes su ciently brittle to be powdered in an iron mortar. Zinc melts at 412° to 415°, and at 940° it boils. It is official under the name of **Zincum,** and this metal should dissolve in dilute hydrochloric or sulphuric acid with evolution of hydrogen, and without leaving an appreciable residue. The purest metal is slowly attacked by sulphuric acid, but the action may be hastened by the addition of a little platinic chloride, to establish galvanic action; the hydrogen evolved should have no disagreeable odor.

Zinc does not readily undergo change when exposed to dry air; in damp air it becomes coated with a thin film of oxide and carbonate, which prevents further action.

Water is not decomposed by zinc at ordinary temperatures, but at 100° slight action takes place, which becomes correspondingly greater as the temperature is increased.

Sodium and potassium hydrates dissolve zinc with evolution of hydrogen and formation of sodium and potassium zincate. Zinc-dust is composed chiefly of a finely-powdered zinc mixed with some oxide. It is a valuable reducing agent in the laboratory, and is used on a commercial scale in the reduction of indigo. It has also some use as a paint.

Uses.—Zinc is used in large quantities in the manufacture of brass. It is also employed in desilvering lead, in galvanizing, in batteries, for roofing, and a great number of other purposes.

ZINC AND THE HALOGENS.

Zinc Chloride, $ZnCl_2$. **Zinci Chloridum,** U.S.P., may be obtained by burning strips of the metal in chlorine gas, and by evaporating the solution of zinc chloride and distilling the residue.

Liquor Zinci Chloridi, U. S. P., is prepared by dissolving the metal in hydrochloric acid to saturation; a small quantity of nitric acid is then added to oxidize any impurity of iron, and the solution is evaporated to a dry mass at a temperature not exceeding 115°. The residue is dissolved in water and allowed to stand in contact with the zinc carbonate for 24 hours; the clear, supernatant liquid is then siphoned off and brought to a strength of 50 per cent.

Since zinc oxide is to be had in commerce of great purity and at a reasonable price, it is probably almost as economical to prepare the chloride by saturating the acid with oxide as follows:

$$ZnO + 2HCl = ZnCl_2 + H_2O.$$

ZnO	$2HCl$	$ZnCl_2$	H_2O
Zinc Oxide.	**Hydrochloric**	**Zinc Chloride.**	**Water.**

The dilute solution of zinc chloride may be filtered through paper, but when more concentrated it should be filtered through asbestos, or allowed to stand until clear and then decanted.

In order to obtain the dry salt, the solution is evaporated in a porcelain dish on a sand-bath until it becomes syrupy, and is then carefully brought to dryness. Some oxychloride is formed during the evaporation, which may be diminished by the cautious addition of hydrochloric acid from time to time. The dried salt may be still further purified by distillation.

Properties.—Zinc chloride is found in commerce as a white. granular powder, or in irregular, porcelain-like masses, or it may be obtained moulded into sticks. It is odorless, intensely caustic, and, when dissolved in sufficient water to make tasting possible, has an astringent, metallic taste. It is very deliquescent ; soluble in 0.3 part of water at 15°, and very soluble in alcohol. When heated to 115° the salt melts, and at a higher temperature it is volatilized with some decomposition, leaving a residue of oxychloride and oxide. The official salt leaves a clear solution with water, and this solution on prolonged boiling deposits a basic salt. The syrupy solution, on the addition of a few drops of hydrochloric acid, deposits octohedral crystals, containing one molecule of water of crystallization. The official solution has a specific gravity of 1.535 at 15°, and reacts acid with litmus paper.

The concentrated, aqueous solution attacks cellulose, and cannot, therefore, be filtered through paper.

Uses.—Zinc chloride in solution is largely used as an antiseptic and disinfectant. It enters into the composition of most embalming fluids, and constitutes the well-known Burnett's disinfecting liquid. A solution of 100 parts of zinc chloride in 12 parts of water, saturated with 6 parts of potassium iodide, and then as much iodine added as the solution will dissolve, furnishes a valuable microscopic reagent for cellulose, with which it gives a blue color. A commercial solution of calamine, zinc blende, or the impure metal in hydrochloric acid, is used to impregnate wood to effect its preservation. The purified salt has some use in medicine as an antispasmodic and alterative, and also as an escharotic.

Zinc Bromide, $ZnBr_2$. **Zinci Bromidum, U.S.P.**—The aqueous solution is easily prepared by gently warming a mixture of zinc, bromine, and water. The same precautions are to be observed, in obtaining the dry salt from this solution, that were noted under the chloride. The dry salt may be purified by sublimation, when it is obtained in white, acicular crystals.

Properties.—Zinc bromide is found as a white, granular powder, odorless, and having a sharp, saline, and metallic taste. It is a very deliquescent salt, readily soluble in water and alcohol. On the application of heat the salt fuses at 394°, and at higher temperatures it sublimes. The aqueous solution reacts acid toward litmus paper.

The chief use of zinc bromide appears to be for the treatment of epilepsy.

Zinc Iodide, ZnI_2. **Zinci Iodidum**, U. S. P.—Zinc and iodine readily unite when heated together, and the salt may, by this process, be obtained in the solid state, which, on heating, yields the salt as a sublimate of white, acicular crystals. A watery solution is obtained by digesting a mixture of 1 part granulated zinc, 3 parts of iodine, and 10 parts of water. When the watery solution is evaporated in a vacuum it yields the salt in octohedral crystals.

Properties.—Zinc iodide occurs as a white, granular powder, odorless, and having a sharp, saline, and metallic taste. It is very deliquescent, and, when exposed to the air, first liquefies, and then absorbs oxygen, with liberation of iodine and the production of a brown color. Water, alcohol, and ether all readily dissolve it. The aqueous solution reddens blue litmus paper. On the application of heat to zinc iodide it melts at about 440°, and at a higher temperature it sublimes with some decomposition, forming quadratic needles, and leaving a residue of zinc oxide.

Zinc iodide has some use in medicine.

ZINC AND OXYGEN.

Zinc Oxide, ZnO. **Zinci Oxidum**, U. S. P.—Zincite, or red oxide of zinc, occurs with other zinc minerals at Mine Hill, New Jersey. Its red color appears to be due to manganese.

Zinc oxide is prepared on a large scale by heating the metal in earthenware retorts; the vapors in contact with air ignite, and are conducted into large chambers, where deposition of the oxide takes place. The product is the commercial zinc white. For pharmaceutical purposes the oxide is usually prepared by heating the basic carbonate to low redness, when the following reaction takes place:

$$\underset{\text{Basic Zinc Carbonate.}}{2ZnCO_3.3Zn(OH)_2} = 5ZnO + \underset{\text{Carbon Dioxide.}}{2CO_2} + \underset{\text{Water.}}{3H_2O.}$$

It is stated that a temperature of 280° to 300° is sufficient to accomplish the above reaction; too high a temperature does not yield as satisfactory a product. The oxide was formerly known as *Lana Philosophica*, *Nihilum Album*, and *Nix Alba*.

Properties.—Zinc oxide is a white, amorphous powder, without odor or taste. It is insoluble in water or alcohol, but is soluble, without effervescence, in dilute acids; it is also soluble in ammonia water, and in solution of ammonium carbonate. When heated zinc oxide becomes yellow in color. It is practically infusible, but in a stream of oxygen, at very high temperatures, it becomes crystalline in character. On exposure to the air it gradually absorbs carbon dioxide.

Uses.—Zinc oxide, when ground with oil, is extensively used as a paint. It has the advantage of not darkening in the presence of sulphur compounds. It is also less injurious to the workmen. It is one of the most economical and satisfactory compounds from which to prepare the various salts of zinc, and is considerably used in medicine.

Zinc Hydrate, $Zn(OH)_2$, is obtained as a white precipitate when sodium or potassium hydrate is added to a solution of zinc sulphate. It is readily soluble in excess of the reagent, forming zincates, as $Zn(ONa)_2$.

When the above zincate solution is boiled the hydrate is thrown down. On immersing a strip of zinc in ammonia water the hydrate is slowly deposited in the form of rhombic prisms, and if a saturated solution of the potassium zincate be allowed to stand for some time octohedral crystals will be deposited, having the formula $Zn(OH)_2.H_2O$.

OXYGEN SALTS OF ZINC.

Zinc Sulphate, $ZnSO_4.7H_2O$. **Zinci Sulphas, U. S. P.**—Under the name of white vitriol this salt was known in the fifteenth century. It was prepared by lixiviation of roasted zinc blende, a process which is used on the large scale at the present time.

The sulphate is also made by dissolving the metal or zinc white in dilute sulphuric acid, and purifying by recrystallization

$$\underset{\text{Zinc Oxide.}}{ZnO} + \underset{\text{Sulphuric Acid.}}{H_2SO_4} = \underset{\text{Zinc Sulphate.}}{ZnSO_4} + \underset{\text{Water.}}{H_2O}.$$

Of course an indefinite amount of water is used in this reaction.

Properties.—Zinc sulphate, containing 7 molecules of water of crystallization, occurs in colorless, transparent, rhombic crystals, without odor, and with an astringent, metallic taste. The crystals effloresce in dry air. The salt is soluble in 0.6 part of water at 15°, and in 0.2 part of boiling water, also soluble in 3 parts of glycerin, but insoluble in alcohol.

It melts in its water of crystallization when rapidly heated, and may be partly decomposed at higher temperatures. On applying heat gradually, 5 molecules of water are driven off at 50° (31.3 per cent.) without melting. At 100° the sixth is lost, and at 110°, in a current of dry air, the salt becomes anhydrous. It loses 6 molecules of water in a vacuum. Monoclinic crystals, containing only 6 molecules of water, may be obtained by having crystallization take place from concentrated solutions and above 30°. A salt having the composition $ZnSO_4.H_2O$ may also be obtained from the hot, concentrated solution. The aqueous solution of zinc sulphate has an acid reaction. Basic salts may be obtained by boiling concentrated solutions of zinc sulphate with metallic zinc or with zinc oxide.

Uses.—Zinc sulphate is used in medicine ; in small doses as a tonic and astringent, in larger doses as an emetic. It has the property, common to all the other zinc salts, of acting as an irritant poison in large doses. The salt is also used in finishing cotton goods.

Zinc Nitrate, $Zn(NO_3)_2.6H_2O$, forms deliquescent crystals when 1 part of zinc oxide is dissolved in 6.5 parts of nitric acid of 25-per-cent. strength. The process by which the metal is dissolved in nitric acid is not employed, since a part of the acid is decomposed and lost in the reaction. The crystals of zinc nitrate form in colorless, striated, four-sided prisms, very soluble in water and in alcohol. When heated, the salt loses nitric acid and becomes converted into a basic nitrate.

Zinc Hypophosphite, $Zn(H_2PO_2)_2.H_2O$, is formed by dissolving zinc oxide in hypophosphorous acid and evaporating. It forms in permanent, rhombohedric crystals.

Zinc Phosphate, $Zn_3(PO_4)_2.4H_2O$, is obtained as a white, nearly insoluble precipitate, by the addition of sodium phosphate solution to a solution of zinc sulphate:

$$2Na_2HPO_4 + 3ZnSO_4 = Zn_3(PO_4)_2 + 2Na_2SO_4 + H_2SO_4.$$

This precipitate is gelatinous when first formed, but becomes crystalline on standing.

Zinc Arsenite, $Zn(AsO_2)_2$, and *Zinc Arsenate*, $Zn_3(AsO_4)_2.3H_2O$, are known. The latter in many respects resembles the phosphate.

Zinc Silicate, Zn_2SiO_4, occurs native as willemite, and the same compound, with 1 molecule of water, occurs as silicious calamine.

Zinc Carbonate. **Zinci Carbonas Præcipitatus**, U. S. P.—This compound is officially defined as "an impalpable powder, of somewhat variable chemical composition." The true c $ZnCO_3$, occurs native as zinc-spar, in hexagonal prisms, sive as smithsonite, hardly to be distinguished from cala may be prepared by precipitating a solution of zinc su the cold with a solution of acid potassium carbonate in

The official basic carbonate is not of constant compos is generally expressed as consisting of 2 molecules of no carbonate and 3 molecules of zinc hydrate, $2ZnCO_3.3Z$

To prepare it, 1 part of sodium carbonate is dissolv parts of water and heated to the boiling point ; to it is th in a thin stream so as not to interfere with the boiling, a of 1 part of zinc sulphate in 10 parts of water. The pr should be such that, after all the zinc solution has bee the mixture has a weak, alkaline reaction. The following the reaction which occurs :

$$\underset{\text{Zinc Sulphate.}}{5(ZnSO_4.7H_2O)} + \underset{\text{Sodium Carbonate.}}{5(Na_2CO_3.10H_2O)} = \underset{\text{Basic Zinc Car}}{2ZnCO_3.3Zn(}$$

$$\underset{\text{Sodium Sulphate.}}{5Na_2SO_4} + \underset{\text{Carbon Dioxide.}}{3CO_2} + \underset{\text{Water.}}{82H_2O.}$$

The precipitate is first washed with hot water by dec and afterwards collected on a filter and washed with until the washings cease to give a reaction with barium

Properties.—Basic zinc carbonate is an impalpable, an powder, permanent in the air, and almost absolutely in water or alcohol ; dilute acids, ammonia water, and so ammonium carbonate dissolve it freely. It is also solubl containing carbon dioxide. At about 300° the salt lo and carbon dioxide, and is converted into zinc oxide, yellow while hot, but becomes white when cold.

Zinc Sulphide, ZnS.—Zinc blende is found native in crysta ing to the regular system, or massive. The color varies fr brown to a deep black, depending on the amount of iron pres also rarely found in nature as the mineral wurtzite, in hexagon

When hydrogen sulphide is passed into a neutral solution of the sulphide is formed as a white, amorphous precipitate. T converted into hexagonal crystals by heating in a current of or when zinc oxide is heated in a current of hydrogen sulphide

Zinc sulphide is soluble in the dilute mineral acids, but in acetic acid.

Zinc Phosphide, Zn_3P_2, **Zinci Phosphidum, U. S.** tained as a gray mass by heating powdered zinc in the phosphorus. It should be preserved in small, glass-stoppered vials. Zinc phosphide is "a gritty powder of a dark gray color, or crystalline fragments of a dark, metallic lustre, and having a faint odor and taste of phosphorus. In contact with the air it slowly emits phosphorous vapor.

"Insoluble in water or alcohol. Soluble in diluted hydrochloric or sulphuric acid with evolution of hydrogen phosphide.

"When strongly heated, with exclusion of air, it melts, and finally sublimes. When heated in air, it becomes oxidized to zinc phosphate."—U. S. P.

Uses.—Zinc phosphide is employed in medicine. Its physiological properties so closely resemble those of phosphorus that it is used as a convenient method of administering that element.

CADMIUM.

Symbol, Cd. *Atomic Weight*, 111.5. *Valence*, II.

History.—Cadmium was discovered in 1817 by Stromeyer of Göttingen. Hermann of Schönebeck discovered it independently and at about the same time.

Occurrence.—Cadmium is found in small quantity in a number of zinc ores, and chiefly as sulphide. The fibrous zinc blende found at Przibram, Bohemia, contains from 2 to 3 per cent. of cadmium. The rare mineral greenockite consists almost entirely of cadmium sulphide. It is found at Bishopstown, in Scotland, at the Ueberoth zinc-mine near Friedensville, in Pennsylvania, and at Granby and Joplin, Missouri.

Preparation.—In the preparation of zinc from ores which contain cadmium the latter metal distils first, and by saving this first portion, mixing it with coal, and distilling it at the lowest possible temperature, a distillate is obtained very rich in cadmium, while the zinc remains behind. This is rendered possible by the boiling point of cadmium being 760°, while that of zinc is 940°. The cadmium is finally separated from the zinc by dissolving in hydrochloric acid, having the latter in slight excess, and passing in hydrogen sulphide; the cadmium sulphide is precipitated, while the zinc remains in solution in the presence of the free acid. The cadmium sulphide is dissolved in hot concentrated hydrochloric acid, and the cadmium precipitated as carbonate by an excess of solution of ammonium carbonate, by which means the copper and arsenic are retained in solution. The cadmium carbonate is washed, dried, and converted by heat into cadmium oxide, which, by distillation with coal, yields the metal.

Properties.—Cadmium is usually found in commerce in sticks. It is a white, lustrous metal, with a fibrous fracture. When pure it is malleable and ductile. Its specific gravity is 8.6 to 8.7. It melts at 320.7°, and boils at 760°. When heated with access of air it burns, giving off a brown vapor. Most of the acids dissolve it readily. Its salts are colorless. In many of their properties the salts of cadmium are identical with those of zinc.

COMPOUNDS OF CADMIUM.

Cadmium Chloride, $CdCl_2.2H_2O$, *Cadmium Bromide*, $CdBr_2.4H_2O$, and *Cadmium Iodide*, CdI_2, are colorless, soluble salts, which are prepared similarly to the corresponding zinc salts. The chloride is made by dissolving the metal or oxide in hydrochloric acid, while the bromide and iodide are prepared by digesting the metal with bromine and iodine respectively in the presence of water. These salts are moderately soluble in alcohol, easily soluble in water, but not deliquescent. They form double salts with the salts of the alkalies, and cadmium potassium iodide, $CdI_2,2KI.2H_2O$, is a useful reagent for alkaloids. Cadmium iodide has some use in photography.

Cadmium Oxide, CdO, forms as a brown, infusible, amorphous powder, when cadmium is burned in the air, or by ignition of the carbonate or nitrate.

Cadmium Hydrate, $Cd(OH)_2$, is prepared by precipitation of a soluble cadmium salt, by potassium or sodium hydrate. It forms, when collected and dried, a white, amorphous powder, which at 300° loses water and is converted into oxide.

Cadmium Sulphate, $CdSO_4$.—This salt was official in the Pharmacopœia of 1870, but since that time it and the other salts of cadmium have practically ceased to have any use in medicine. To prepare this salt, 10 parts of cadmium in small pieces are placed in a porcelain dish with 10 parts of pure sulphuric acid and 40 parts of water. The mixture is warmed until solution is effected, and the solution is filtered and evaporated to crystallize. On account of the slowness with which sulphuric acid acts on cadmium, the metal is sometimes first dissolved in nitric acid, and the hydrate is precipitated from the resulting nitrate by sodium hydrate, and then dissolved in the sulphuric acid.

Properties.—Cadmium sulphate crystallizes in large, colorless, monoclinic crystals, having the composition $3CdSO_4.8H_2O$. They are permanent in the air, easily soluble in water, and the aqueous solution has an acid reaction. The sulphates of the alkalies and of the alkaline earths yield with cadmium sulphate well-crystallized double salts. It has been used as an astringent in diseases of the eye.

Cadmium Nitrate, $Cd(NO_3)_2.4H_2O$, is obtained by dissolving the metal in nitric acid. It crystallizes in fibrous needles, which are very deliquescent, and are, therefore, very soluble in water; soluble also in alcohol.

Cadmium Carbonate.—The normal salt $CdCO_3$ appears not to be known. The basic salt is obtained by precipitating solution of cadmium sulphate with sodium carbonate. It has a variable composition, and in other respects resembles the corresponding zinc salt.

Cadmium Sulphide, CdS, is obtained as a yellow powder, insoluble in hydrochloric acid. It is used as a pigment under the names of *King's yellow* and *jaune brillant*.

CHAPTER IV.

THE SILVER GROUP.

SILVER (Argentum).

Symbol, Ag. *Atomic Weight*, 107.66. *Valence*, I.

History.—Silver was one of the earliest known metals. It was the *Luna* or *Diana* of the alchemists.

Occurrence.—Native silver is found to some extent; large masses have been found in Norway, in Peru, and in Western United States. In the Lake Superior district it occurs associated with copper, but not alloyed with it, which points to the fact that deposition has taken place from solution. In combination silver occurs most abundantly as sulphide, argentite, or silver glance, Ag_2S. In other minerals it is associated with lead, copper, antimony, gold, and mercury. The rarer minerals containing silver are the combinations of it with the halogens, chlorine, bromine, and iodine; the compound with chlorine is known as horn silver. Small quantities of silver occur in nearly all lead ores, and although the amount appears to be small, nevertheless the quantity extracted from this source is very considerable. Silver occurs in sea water, and in the ash of some land plants.

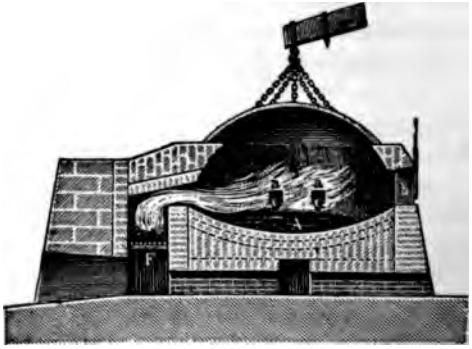
Extraction.—Metallic silver is extracted from its ores by several different processes, the most important of which are: (1) *The Cupellation Process*, (2) *The Amalgamation Process*, (3) *Extraction in the Wet Way*, (4) *Electrolytic Process*.

(1) *The Cupellation Process* is the oldest, and, with modifications to suit the ores in different localities, it is still in use. It is employed in the separation of silver from lead. When the lead is sufficiently rich in silver it is cupelled at once, but oftener it is necessary first to remove the large excess of lead; this is accomplished by the Pattinson process, which consists in melting the lead in an iron vessel and allowing it to cool slowly. Crystals of pure lead first separate, which are constantly removed by perforated ladles, and this is continued until but one-third of the metal in the pot remains. If then it is sufficiently rich in silver it is removed and cupelled. Instead of removing the excess of lead by Pattinson's process, the metal may be melted and zinc added in about the proportion of 18 parts of zinc for every 1 part of

silver present. The zinc alloys with the silver, rises to the top, and may be removed as a solid cake. This cake is then heated to redness in a current of air, by which the zinc is oxidized, and may be removed from the silver by washing with water.

The alloy of silver and lead obtained in the above processes is fused on the hearth of a reverberatory furnace, the bottom of which is covered with bone-ash or with a kind of clay. Such a furnace is shown in section in Fig. 74. *F* is the furnace, *A* the hearth, *a a* entrances for the blast of air, and *b* the working door. A rapid current of air is introduced over the molten metal on the hearth, by which the lead is oxidized, and either flows off through lateral openings or is skimmed off by workmen through the door *b*. Towards the end of the operation, the temperature is raised from a dark-red to a cherry-red heat, the surface of the metal is covered with iridescent films, but at last they disappear, and the metal then takes on the brilliant silver appearance known as *fulguration*. Fig. 75 shows an exterior view of the same furnace, *g* in this case being the working door, through which access is gained to skim the oxide from the metal.

FIG. 74.



Silver cupellation furnace, cross-section.

(2) *The Amalgamation Process* varies somewhat according to the locality in which it is conducted. That formerly employed at Freiberg consists in roasting the finely-ground ore with common salt, on the floor of a reverberatory furnace; the mass is then again ground very fine, placed in a cask with scrap-iron and water, and agitated by machinery. The silver ore is converted into chloride in the roasting process, and this reacts when brought in contact with the iron as follows:

$$\underset{\text{Silver Nitrate.}}{2AgNO_3} + \underset{\text{Sodium Hydrate.}}{2NaOH} = \underset{\text{Silver Oxide.}}{Ag_2O} + \underset{\text{Sodium Nitrate.}}{2NaNO_3} + \underset{\text{Water.}}{H_2O.}$$

The precipitate is first washed by decantation, then on a filter, until the washings cease to give a reaction for nitric acid, and finally dried in the dark at ordinary temperatures.

Properties.—Silver oxide is a heavy, dark-brown or black powder, according to the method of preparation; the darker product is obtained when precipitation has taken place from hot concentrated solutions, or when the drying has been conducted at temperatures at or above 70°. It is slightly soluble in water, to which it imparts an alkaline reaction, insoluble in alcohol, and completely soluble in nitric acid without effervescence. The aqueous solution, in addition to its alkaline reaction, has a metallic taste, and may be assumed to contain silver hydrate, AgOH. When heated to 250° or 300°, it is decomposed into metallic silver and oxygen.

In the freshly-precipitated, moist condition silver oxide is more active than the same compound after it has been dried and then moistened. In the freshly-precipitated state it decomposes soluble chlorides, precipitates oxides from many metallic salts, and absorbs carbon dioxide from the air.

Silver oxide should not be triturated with antimony sulphide, arsenic sulphide, precipitated sulphur, amorphous phosphorus, tannin, or other easily oxidizable substances, since such mixtures readily inflame. Silver oxide is soluble in concentrated solution of ammonia, and on diluting this solution with water, black crystals of ***ammonio-silver oxide*** (Berthollet's fulminating silver) separate; these on drying become very explosive; for this reason the precaution should be observed not to bring silver oxide in contact with ammonia.

Silver oxide has some use in medicine, but its greatest value is as a laboratory reagent, where it is employed in the freshly-precipitated condition.

Silver Peroxide, Ag_2O_2, is also known, having been obtained by electrolysis of the nitrate in solution. It should not be brought in contact with sulphur, phosphorus, organic substances, or ammonia. On the application of heat it decomposes into oxygen and the metal.

OXYGEN SALTS OF SILVER.

Silver Chlorate, $AgClO_3$, is prepared by dissolving silver oxide in chloric acid. It forms small, quadratic crystals, soluble in 10 parts of water. Rapid heating, pressure, or concussion causes the salt to explode.

water, common salt, copper sulphate, and mercury is used; the mixing is almost invariably accomplished by mules, with intervals of allowing it to stand, so that from two weeks to two months are frequently required to effect the amalgamation of the silver.

(3) *Extraction in the Wet Way* is accomplished, according to Ziervogel's process, by roasting the ores, which usually contain sulphur, iron, and copper, at such a temperature that the sulphates of iron, copper, and silver, which are formed, are not all decomposed, but only the salts of iron and copper. The mass is then lixiviated with water, which dissolves the silver sulphate and leaves the insoluble oxides of iron and copper behind. The silver is removed from the solution by precipitation with metallic copper. A modification of this process consists in roasting with common salt, whereby silver chloride is formed, and is washed out from the mass by a solution of sodium thiosulphate; from this solution the silver is precipitated as sulphide by sodium sulphide, and the silver sulphide is reduced to metal by heating to a high temperature in a current of air.

(4) *The Electrolytic Process.*—This method is used to separate silver from the native copper and copper oxide with which it occurs. The two poles, one of native copper oxide, CuO, and the other of native copper, are immersed in a bath of acid copper sulphate, and a strong current from a dynamo is sent through the solution, whereby the noble metals are dissolved from the copper oxide and deposited on the anode in powder. This process has not been developed to that degree to secure for it any extended use as yet.

Preparation of Pure Silver.—The metal obtained by the above processes is still contaminated with copper, and sometimes also with gold and platinum. To effect its purification, it is dissolved in nitric acid, which leaves gold undissolved, and from this filtered solution the silver is precipitated by hydrochloric acid. The washed and dried chloride is fused with an excess of sodium carbonate, and the pure metal collects at the bottom of the crucible.

Another method consists in reducing the chloride by laying it on plates of zinc and covering it with dilute hydrochloric acid. The metal is thereby obtained in a finely-divided state, in which form it has some uses in the laboratory.

Properties.—Silver is a pure white, lustrous metal, capable of taking a high polish. In some conditions, for instance, that in which it is obtained from some organic silver salts, it has a white, porcelain-like color, owing to the roughness of its surface, and is devoid of lustre.

The native silver is sometimes found in small crystals of the regular system. Of all the metals silver is the best conductor of heat and electricity. In hardness it stands between copper and gold. In malleability and ductility it is inferior only to gold; it has been beaten into leaf 0.00025 millimeter in thickness, and drawn into wire of such fineness that 180 metres weigh 0.1 gramme. In very thin films, as when deposited on glass from solution, it transmits blue light. Ordinarily the specific gravity of silver is 10.424, but when distilled it has a specific gravity of 10.575.

Silver fuses at a temperature of about 1040°, and at an intense white heat, such as is obtained from the oxyhydrogen lamp, it distils. When melted in air, pure silver absorbs 22 times its volume of oxygen, which it gives out again at the moment of solidification; this is sometimes accompanied with the projection of small particles of the metal, and is termed the *spitting of silver.*

When exposed to the atmosphere or to water, silver remains unchanged, but in the presence of a small quantity of ozone it becomes coated with a thin layer of oxide. The darkening, which sometimes takes place when silver is exposed to the air, is due to small quantities of hydrogen sulphide.

Nitric acid is the best solvent of silver. The compact metal is only slightly attacked by hydrochloric or dilute sulphuric acid even at the boiling temperature. In the presence of potassium permanganate the metal is dissolved by dilute sulphuric acid.

The finely-divided metal is slightly attacked by hydrochloric acid with evolution of hydrogen and formation of silver chloride; hydriodic acid acts more energetically upon it. Concentrated sulphuric acid dissolves silver with evolution of sulphur dioxide and formation of silver sulphate.

The alkalies have little or no action on silver; potassium or sodium hydrate may be fused with it, and fused potassium nitrate has but little action upon it.

Uses.—The pure metal is used to prepare the salts of silver, and in the manufacture of certain utensils for pharmaceutical and chemical purposes, as crucibles, dishes, wire, foil, etc. For many of the purposes to which silver is applied it is too soft to resist wear, and in order to increase its hardness it is alloyed with copper in various proportions. In the United States, France, Germany, and Austria the proportion of copper is 10 per cent., and such an alloy is used in those countries for coinage. In England the proportion employed is 7.5 per cent. of copper.

The term *fineness* applied to silver indicates the parts per thousand of pure silver in the alloy; for instance, in this country silver coin is spoken of as "900 fine;" that is, 90 per cent. silver and 10 per cent. copper.

Electroplating.—This is a process in which a thin layer of silver is deposited on metallic surfaces by electrolysis. The object to be coated must have a conducting surface, and is made the negative pole; a bar of silver acts as the positive pole. These electrodes are placed in a solution of silver cyanide in an excess of potassium cyanide. If the object to be coated is properly cleaned, the silver will be deposited on it as a coherent layer; at the same time cyanogen is liberated at the positive pole and dissolves the silver, thereby keeping the silvering solution of constant strength.

The silvering solution used in electroplating is made by dissolving 1 part of silver nitrate in 50 parts of distilled water and mixed with a solution of 5 parts of potassium cyanide in 20 parts of distilled water.

Silvering on Glass.—When alkaline solutions of silver salts are mixed with certain organic compounds like grape-sugar, Rochelle salt, etc., the silver is deposited on the surface of the vessel in which it is contained as a thin, coherent film. The following process will yield satisfactory results if the glass be first thoroughly cleaned with alkali, and then washed with distilled water:

Dissolve 7.8 grammes of silver nitrate in 60 c.c. of water, and divide the solution in two equal portions. Dissolve, also, 3.1 grammes of Rochelle salt in 1180 c.c. of water, and heat the solution to the boiling point. Add to it gradually (so as not to stop the ebullition) one of the portions of silver solution, boil some 10 minutes longer, cool, and decant the clear liquid. To the other half of the silver solution add just sufficient ammonia water to dissolve the precipitate which is first formed, or only leave a faint cloudiness; then add 360 c.c. of water and filter. Equal portions of these two solutions, when mixed and poured on glass, will deposit a brilliant coating of silver in about 10 minutes, according to the temperature of the room. The coating of silver should then be well washed, dried, and varnished. Plating is also accomplished by a number of mechanical processes.

The production of silver for the year 1893 in the United States amounted to 60,500,000 troy ounces, valued at $78,220,450 at the mines; this is about 40 per cent. of the output of the whole world.

SILVER AND THE HALOGENS.

Silver Chloride, AgCl, is found native as kerargyrite, or horn silver, in Mexico, Peru, Chili, and in various parts of Germany. It occurs in crystals of the regular system or in pearl-gray, translucent, wax-like masses. Sea water contains a small quantity of silver chloride.

Preparation.—Pure silver chloride is prepared by precipitating a solution of silver nitrate with pure hydrochloric acid. The precipitate is of a more or less cheesy consistence, but boiling or long standing causes it to become more granular; it is collected and washed until the washings cease to have an acid reaction. The whole process should be conducted with exclusion of light.

Properties.—The artificially-prepared salt is a white, amorphous, insoluble powder. The insolubility in water and dilute acids is so complete as to make the chloride the best salt by which to determine silver quantitatively. When freshly prepared, it is readily soluble in ammonium hydrate, in solutions of sodium thiosulphate, potassium cyanide, and concentrated mercuric and mercurous nitrate. On the application of heat, silver chloride melts at 260° to a thick, yellow liquid, which becomes a tough, solid mass on cooling. When exposed to light the salt rapidly darkens, with loss of chlorine. Dry silver chloride absorbs at ordinary temperatures 19 per cent. of its weight of gaseous ammonia, forming the ammonio-silver chloride, $AgCl,2NH_3$, a white compound, which at 37.7° gives off the ammonia.

Use.—Silver chloride finds some use in photography.

Silver Bromide, AgBr, occurs native as bromargyrite in Mexico and Chili. The bromide is prepared similarly to the chloride, by precipitating silver nitrate with hydrobromic acid or potassium bromide. It has a faint yellow color, and has the solubilities and many of the properties of the chloride. It is not easily soluble, however, in ammonium hydrate, and the dry bromide does not absorb ammonia; an ammonio-silver bromide is formed by allowing the ammoniacal solution to stand for some time. Silver bromide is largely used in photography.

Silver Iodide, AgI. **Argenti Iodidum**, U. S. P.—This salt occurs native as the mineral iodargyrite, in Mexico, Chili, Spain, and Arizona, in the form of thin, slightly elastic, hexagonal tables.

Preparation.—Silver iodide may be prepared in a variety of ways, by direct union of the elements, by dissolving silver in hydriodic acid, etc., but it is most readily and economically obtained by adding a solution of potassium iodide to one of silver nitrate, collecting, washing, and drying the precipitate without exposure to light. It should be preserved in dark amber-colored vials.

Properties.—Silver iodide is a heavy, yellowish, amorphous powder, without odor or taste. It is insoluble in water, dilute acids, or solution of ammonium carbonate; soluble in 2500 parts of stronger ammonia water. It is also dissolved by an aqueous solution of potassium cyanide, and by a concentrated solution of potassium iodide.

On the application of heat, silver iodide melts at 400° to a dark-red liquid, which, on cooling, congeals to a soft, yellow, translucent mass. The dry precipitated compound absorbs 3.6 per cent. of ammonia gas, forming the white compound $AgI,2NH_3$, which on exposure to air gives off ammonia and becomes yellow.

Like the chloride and bromide, silver iodide has considerable use in photography. It also has some use in medicine, probably on account of the claim made that it does not discolor the skin like the other silver salts.

Silver Fluoride, AgF, is obtained by dissolving silver oxide or carbonate in hydrofluoric acid. The resulting solution is concentrated in a platinum dish in a vacuum, with exclusion of light. It deposits crystals with 1 or 2 molecules of water, according to the degree of concentration at which crystallization takes place. It is a deliquescent salt, soluble in one-half its weight of water.

SILVER AND OXYGEN.

Silver Suboxide, Ag_4O, *Argentous Oxide*, is obtained by the action of hydrogen on certain salts of silver, preferably the citrate. When silver citrate is heated to 100°, and then subjected at that temperature to the action of hydrogen, a black mass is formed, which, on dissolving in water and treating with potassium hydrate, yields argentous oxide. This has a dark, metallic lustre, and decomposes on heating into oxygen and silver.

Silver Oxide, Ag_2O. *Argentic Oxide*, **Argenti Oxidum**, U. S. P.—A solution of 10 parts of silver nitrate in 100 parts of water is treated with solution of sodium hydrate so long as a precipitate is formed:

$$\underset{\text{Silver Nitrate.}}{2AgNO_3} + \underset{\text{Sodium Hydrate.}}{2NaOH} = \underset{\text{Silver Oxide.}}{Ag_2O} + \underset{\text{Sodium Nitrate.}}{2NaNO_3} + \underset{\text{Water.}}{H_2O}.$$

The precipitate is first washed by decantation, then on a filter, until the washings cease to give a reaction for nitric acid, and finally dried in the dark at ordinary temperatures.

Properties.—Silver oxide is a heavy, dark-brown or black powder, according to the method of preparation; the darker product is obtained when precipitation has taken place from hot concentrated solutions, or when the drying has been conducted at temperatures at or above 70°. It is slightly soluble in water, to which it imparts an alkaline reaction, insoluble in alcohol, and completely soluble in nitric acid without effervescence. The aqueous solution, in addition to its alkaline reaction, has a metallic taste, and may be assumed to contain silver hydrate, AgOH. When heated to 250° or 300°, it is decomposed into metallic silver and oxygen.

In the freshly-precipitated, moist condition silver oxide is more active than the same compound after it has been dried and then moistened. In the freshly-precipitated state it decomposes soluble chlorides, precipitates oxides from many metallic salts, and absorbs carbon dioxide from the air.

Silver oxide should not be triturated with antimony sulphide, arsenic sulphide, precipitated sulphur, amorphous phosphorus, tannin, or other easily oxidizable substances, since such mixtures readily inflame. Silver oxide is soluble in concentrated solution of ammonia, and on diluting this solution with water, black crystals of *ammonio-silver oxide* (Berthollet's fulminating silver) separate; these on drying become very explosive; for this reason the precaution should be observed not to bring silver oxide in contact with ammonia.

Silver oxide has some use in medicine, but its greatest value is as a laboratory reagent, where it is employed in the freshly-precipitated condition.

Silver Peroxide, Ag_2O_2, is also known, having been obtained by electrolysis of the nitrate in solution. It should not be brought in contact with sulphur, phosphorus, organic substances, or ammonia. On the application of heat it decomposes into oxygen and the metal.

OXYGEN SALTS OF SILVER.

Silver Chlorate, $AgClO_3$, is prepared by dissolving silver oxide in chloric acid. It forms small, quadratic crystals, soluble in 10 parts of water. Rapid heating, pressure, or concussion causes the salt to explode.

Silver Bromate, $AgBrO_3$, and *Silver Iodate*, $AgIO_3$, are difficultly soluble, white, crystalline precipitates, obtained by treating solution of silver nitrate with potassium bromate or iodate.

Silver Sulphite, Ag_2SO_3, is obtained as a white, cheesy precipitate when sulphurous acid is added to a solution of silver nitrate. On heating to 100°, it decomposes into silver and silver sulphate.

Silver Sulphate, Ag_2SO_4, is prepared by dissolving silver in concentrated sulphuric acid, or by adding sulphuric acid to an alcoholic solution of silver nitrate.

It forms in small, lustrous, rhombic crystals, which are isomorphous with anhydrous sodium sulphate. It is soluble in 200 parts of cold water and in 70 parts of boiling water; insoluble in alcohol. Concentrated sulphuric acid dissolves the salt, and it is precipitated by dilution with water. At a red heat silver sulphate melts without decomposition, and at higher temperatures it is resolved into metallic silver, sulphur dioxide, and oxygen.

Silver sulphate is obtained in considerable quantities in the commercial separation of silver from gold by means of sulphuric acid, and is used to furnish pure silver.

Acid Silver Sulphate, $AgHSO_4$, is formed by dissolving silver sulphate in hot, concentrated sulphuric acid, and allowing the solution to cool.

Silver Pyrosulphate, $Ag_2S_2O_7$, results when silver sulphate is heated with sulphur trioxide.

Silver Thiosulphate, $Ag_2S_2O_3$, is also known.

Silver Nitrite, $AgNO_2$.—On mixing warm, concentrated solutions of 16 parts of silver nitrate and 10 parts of potassium nitrite, a crystalline precipitate of silver nitrite results. It has some use in the preparation of other nitrites.

Silver Nitrate, $AgNO_3$. **Argenti Nitras,** U. S. P.—This salt was first obtained in the crystalline form by Geber, in the eighth century. It came into medical use in the seventeenth century, under the names of *magisterium argenti*, *crystalli dianæ*, and when cast into sticks as *lapis infernalis* and *lunar caustic*.

A pure silver should be selected for the preparation of the nitrate; that made from the sulphate answers this purpose very well. In a capacious porcelain dish 3 parts of metallic silver are mixed with 10 parts of nitric acid (containing 25 per cent. HNO_3), and the mixture warmed until the reaction begins. In case the silver is finely divided, the action is sufficiently active without warming, and may have to be controlled by the addition of a little cold water:

$$3Ag + 4HNO_3 = 3AgNO_3 + 2H_2O + NO.$$

A funnel should be inverted over the liquid in the dish to prevent particles of the acid and solution from flying out, and when the action ceases, the silver being dissolved, the sides of the funnel are rinsed down with distilled water; the solution is filtered through glass wool, if necessary, and evaporated on a sand-bath to dryness. The temperature is then raised so as to melt the salt and complete the escape of nitrous fumes, which is soon accomplished when the salt is pure; but when it contains copper nitrate it takes somewhat longer, and the copper is converted into insoluble oxide, as follows:

$$Cu(NO_3)_2 = CuO + 2NO_2 + O.$$

The reaction is known to be ended when there is no further evolution of gas, and the mass becomes dark or black from the formation of the copper oxide.

The fused mass is dissolved in double its weight of water, filtered through a small, well-washed filter, and set aside to crystallize; dust and light should be excluded as far as possible during the operation. In case lunar caustic is wanted, the fused silver nitrate is treated with a few drops of nitric acid to oxidize any nitrite, and after a few moments more heating, is poured into polished iron moulds such as are used in the preparation of sticks of sodium or potassium hydrate; see Fig. 60, page 301. It is preferable to have such moulds gold-plated.

Properties.—Silver nitrate occurs in colorless, transparent, tabular, rhombic crystals, permanent in the air, but becoming gray or grayish-black on exposure to light in the presence of organic matter. It is without odor, but has a bitter, caustic, and metallic taste.

The salt is soluble in 0.6 part of water at 15°, and in 0.1 part of boiling water; also soluble in 26 parts of cold and in 5 parts of boiling alcohol.

On the application of heat, the salt melts at about 200° without decomposition, and on cooling forms a white, crystalline mass. If kept for some time at a temperature above 210° it begins to decompose with formation of silver oxide and silver nitrite. At a red heat decomposition takes place, nitrous fumes, nitrogen, and oxygen being evolved and metallic silver remaining. The aqueous solution of silver nitrate is neutral to litmus paper.

Solution of ammonia added to a solution of silver nitrate at first produces a precipitate which in the presence of a larger amount of the reagent dissolves; if this solution then be allowed to evaporate, rhombic, prismatic crystals separate, having the composition $AgNO_3,2NH_3$. When heated above 100° they melt, evolving nitrogen and ammonia, leaving a residue of ammonium nitrate and a mirror of metallic silver.

Uses.—Silver nitrate is largely used as a laboratory reagent and in photography. It also has considerable use in medicine as a cautery, its employment internally being limited; when used internally for some time it produces a peculiar bronze coloration of the skin.

For external use there are two preparations of silver: **Argenti Nitras Fusus**, U. S. P., and **Argenti Nitras Dilutus**, U. S. P., which are usually employed. The fused nitrate, or *lunar caustic*, contains a small quantity of silver chloride in order to toughen it; this is accomplished by adding to 100 grammes of the salt 4 grammes of hydrochloric acid, melting the mixture at as low a temperature as possible, and pouring into suitable moulds. The diluted silver nitrate, or ***mitigated caustic***, is made by melting at the lowest possible temperature 30 grammes of silver nitrate and 60 grammes of potassium nitrate, and casting in suitable moulds.

Silver Phosphate, Ag_3PO_4, is obtained when the normal sodium phosphate or the disodium hydrogen phosphate is added to a solution of silver nitrate. It is a yellow, amorphous compound, insoluble in water, soluble in nitric acid and in ammonia. It dissolves in concentrated phosphoric acid on warming, with the formation of the compound Ag_2HPO_4.

Compounds of silver with pyrophosphoric acid and with metaphosphoric acid are also known.

Silver Carbonate, Ag_2CO_3, is obtained by adding sodium carbonate to silver nitrate solution, collecting and washing the precipitate. It is a yellow, amorphous powder, insoluble in water; soluble in nitric acid and in ammonia. It turns black on exposure to air and light, and at 200° decomposes into silver oxide and carbon dioxide.

Silver Sulphide, Ag_2S, is found native as argentite or vitreous silver, in grayish-black crystals of the regular system. It can be obtained artificially by igniting silver chloride in a current of hydrogen sulphide.

Much of the so-called ***oxidized silver*** is coated with a thin layer of sulphide, obtained by heating together silver and solution of potassium sulphide. A more permanent result is obtained by coating the silver with platinic chloride solution. In both cases considerable washing and polishing are necessary to get a good result.

GOLD (Aurum).

Symbol, Au. *Atomic Weight*, 196.7. *Valence*, I and III.

History.—Gold has been known from the earliest times. On account of its scarcity, its color, and its stability in contact with air, it early became an important metal from which to make jewelry, certain household utensils, and money.

Occurrence.—Gold is very widely distributed in nature, but always in small quantities. It is ordinarily found in the free or uncombined state; rarely it is found amalgamated with mercury or combined with tellurium.

In the free state it is frequently in a crystalline condition, the commonest forms being the octohedron or tetrahedron; occasionally the elongated forms of these give it the appearance of being acicular.

The native deposits are usually in veins of quartz, although the usual source of the metal is in alluvial soils resulting from the disintegration of the rocks in which it was imbedded. It is found in the sand of most rivers and in sea water.

Gold is rarely found in a pure condition, it being usually mixed with silver, and more rarely with copper, iron, and platinum; when it contains more than 36 per cent. of silver it is termed *electrum*.

The principal localities in which gold is found in sufficient quantity to extract are the gold-fields of Western United States, Australia, Siberia, Transylvania, Brazil, New Zealand, and South Africa.

The United States in 1893 produced 1,739,081 troy ounces, valued at $35,950,000. This was not far from 30 per cent. of the output of the whole world.

Extraction.—Most of the gold is obtained by a process of levigation, in which sand and alluvial deposit from gold-bearing rocks are washed with water, the lighter portions being allowed to run off, while the heavier portions with the gold remain and are intimately mixed with mercury, so that an amalgam of gold and mercury is formed, from which the latter is distilled. This is a very brief outline of the process, which has innumerable modifications; for instance, it may be carried out by one man with a pan, when it is termed *pan-washing*; or a little more elaborate apparatus may be employed, requiring the attention of four men, when it is termed *cradle-washing*; or, finally, *hydraulic mining* may be used. The last consists in washing large quantities of earth by means of water brought from higher situations in the mountains, so that enormous quantities may be employed. The water and earth are run through a long series of troughs, cut in the rock, and in these troughs depressions are cut at intervals termed "sluice-boxes," in which small quantities of mercury are placed, so that the gold is taken out by it. In addition to the boxes, plates of copper coated with mercury are often placed in the troughs to arrest the finer particles of gold; these plates are removed from time to time, the surface scraped, and, after re-amalgamation, returned.

When quartz rock is worked, it is first reduced to a fine powder by mechanical processes, and then washed.

The *chlorine process* is sometimes used, especially where the metal i associated with pyrites. The ore is first roasted, then mixed with wate in tubs, and saturated with chlorine; this is allowed to stand 10 to 1 hours, when the gold passes into solution; the solution containing gol chloride is run off and treated with ferrous sulphate, which precipitate the metallic gold in the form of a fine powder, which is collected an fused to a globule with borax.

Gold prepared by the above processes contains silver, copper, or platinum,—sometimes all three. When the proportion of gold does not exceed 33 per cent. the silver of the alloy may be dissolved by nitric acid o specific gravity 1.320; this was formerly known as *quartation*, because i was believed that an alloy must not contain over 25 per cent. gold i order for the silver to be dissolved by the acid. When the gold in th alloy exceeds 33 per cent. it is fused with sufficient silver to reduce i to that proportion, when the silver can be removed by nitric acid. Sulphuric acid is used in the same way to separate gold. An alloy may contain 25 per cent. gold and 10 per cent. copper; the acid should have a specific gravity of 1.840. The operation is conducted in cast-iron boiler with leaden domes; the sulphur dioxide which is evolved may either b allowed to escape or be conducted into chambers for the manufacture o sulphuric acid.

When a sample of gold does not contain more than 10 per cent. o silver, it is fused in a clay crucible, which has been glazed on the insid with borax, and a stream of chlorine is passed into the molten metal silver chloride forms and rises to the top, a layer of borax prevents i from volatilizing; the chlorides of zinc, bismuth, arsenic, and antimony when present, are volatilized. A final purification is sometimes given t the gold, after removal of silver, by dissolving it in nitrohydrochlori acid, evaporating on a water-bath to a syrupy consistence, mixing thi with some 20 times its volume of water, filtering, and treating the filtrat with solution of ferrous chloride, when metallic gold is precipitated according to the following reaction:

$$\begin{array}{ccccccc} 2AuCl_3 & + & 6FeCl_2 & = & 2Au & + & 3Fe_2Cl_6. \\ \text{Gold Chloride.} & & \text{Ferrous Chloride.} & & \text{Gold.} & & \text{Ferric Chloride.} \end{array}$$

Oxalic acid or ferrous sulphate may be used to effect this precipitatio of the gold.

Properties.—In the compact state gold has a characteristi yellow color, a peculiar lustre, and is capable of a high polish. I the precipitated condition it is a brown powder. The native gol occurs in small cubical or octohedral crystals, and sometimes i other forms of the regular system. It is the most malleable and ductile of the metals; in very thin leaves it transmits a green light. When pure it is nearly as soft as lead. The specific gravity varies, according to its mode of preparation or treatment, from 19.26 to 19.55. On the application of heat it melts at 1240° to a bluish-green liquid.

Chlor-auric Acid, $AuCl_3,HCl.4H_2O$, is one of the double compounds with hydrochloric acid. It is formed when hydrochloric acid is added to a solution of auric chloride, and the whole is allowed to evaporate slowly over quick-lime; long, yellow crystals are deposited, which rapidly deliquesce on exposure to the air. This compound forms a series of salts termed *chlor-aurates*, or they may simply be considered double compounds of auric chloride with the salt; the best known of these is *sodium chloraurate*, or *gold* and *sodium chloride*. This compound is prepared by dissolving gold in a mixture of nitric and hydrochloric acids, and evaporating the solution on a water-bath to a syrupy consistence:

$$\underset{\text{Gold.}}{2Au} + \underset{\text{Hydrochloric Acid.}}{8HCl} + \underset{\text{Nitric Acid.}}{2HNO_3} = \underset{\text{Chlor-auric Acid.}}{2AuCl_3,HCl} + \underset{\text{Nitric Oxide.}}{2NO} + \underset{\text{Water.}}{4H_2O.}$$

The proportions are 10 parts of gold to 13 parts of nitric acid of 25 per cent., and 32 parts of hydrochloric acid of 25 per cent. The syrupy solution of chlor-auric acid is treated with a solution of 4 parts of pure sodium chloride in 60 parts of water, and the resulting mixture evaporated until a pellicle forms; evaporation being completed at ordinary temperatures over quick-lime:

$$\underset{\text{Chlor-auric Acid.}}{AuCl_3,HCl} + \underset{\text{Sodium Chloride.}}{NaCl} = \underset{\text{Gold and Sodium Chloride.}}{AuCl_3,NaCl} + \underset{\text{Hydrochloric Acid.}}{HCl.}$$

The **Auri et Sodii Chloridum,** U. S. P., is a mixture prepared by rubbing together equal parts of dry gold chloride and sodium chloride. Theoretically it contains 32 per cent. of metallic gold, although the official requirements are simply that it shall contain not less than 30 per cent. of this metal.

The true gold and sodium chloride has the formula $AuCl_3,NaCl.2H_2O$, and contains 50 per cent. of metallic gold. It occurs in orange-yellow, rhombic tables or prisms, is deliquescent, and when exposed to a red heat decomposes, leaving a residue of metallic gold.

This compound is used in photography, for gilding, and to some extent in medicine.

Auric Bromide, $AuBr_3$ (Gold Tribromide), *Auric Dibromide*, $AuBr_2$, and *Auric Iodide*, AuI_3, are known.

GOLD AND OXYGEN.

Aurous Oxide, Au_2O, is a dark-violet powder, obtained by treating aurous chloride with potassium hydrate in the cold.

Auric Oxide, Au_2O_3, is a dark-brown powder, formed by heating auric hydrate to 100°. Strong heat decomposes it into gold and oxygen.

Auric Hydrate, $Au(OH)_3$, *Gold Hydroxide*, *Auric Acid.*—This compound is best prepared by heating a solution of auric chloride with magnesia, and washing the precipitate with dilute nitric acid. When freshly prepared it is a yellowish-brown precipitate, which on drying becomes a brown powder. Auric hydrate is acid-forming, and its salts are termed aurates. When it is treated with an excess of ammonia water, a green to brown powder is formed, known as *fulminating gold.* In the dry state this ammonia compound explodes violently, either by percussion or on heating.

AURATES.

Potassium Aurate, $KAuO_2.3H_2O$, is the only one of these compounds that has been investigated. It is obtained by dissolving auric hydrate in potassium hydrate solution, and evaporating the resulting solution in a vacuum. It forms in small, yellow, acicular crystals, which are readily soluble in water and have a strong alkaline reaction. It is used in gilding copper and some other metals.

CHAPTER V.

THE COPPER AND MERCURY GROUP.

COPPER.

Symbol, Cu. *Atomic Weight*, 63.18. *Valence*, $(R_2)^{II}$ and II.

History.—Copper, because of its rather abundant occurrence in the metallic state, was probably the first metal used by man. It formed the material for tools and weapons before the metallurgical processes necessary to produce iron were known. Originally copper was found in the island of Cyprus, and on this account its name gradually came to be *cuprum*.

Occurrence.—The most abundant occurrence of native copper is in the State of Michigan, in what is known as the Lake Superior district. Valuable ores of copper are found in Cornwall, England, in Siberia, and in the Ural. Spain, Chili, Peru, Japan, and Australia also produce considerable quantities. One of the most abundant ores of copper is cuprous oxide, Cu_2O, or red copper ore; cupric oxide, CuO, is found more rarely. The sulphide, or copper glance, Cu_2S, is also widely distributed. Smaller quantities occur as malachite, or copper carbonate, $CuCO_3,Cu(OH)_2$. Bornite and chalcopyrite are mixed sulphides of copper and iron, and are very widely distributed.

Extraction.—The method of obtaining copper from its ores depends on whether the ore is an oxide or sulphide. If an oxide or a carbonate, the ore is simply heated with charcoal or other fuel, with, perhaps, the addition of some flux rich in silica. This process is much employed in the United States. Usually, however, the ore is a sulphide mixed with iron sulphide, lead, antimony, and silver; often not more than 13 per cent. of copper is present. The ore is first roasted on the floor of a reverberatory furnace, the air-supply being controlled by suitable apertures. In this way the sulphides are partly converted into oxides. The roasted ore is next fused with a silicious flux, to which fluor-spar is sometimes added to increase its fusibility. The temperature for this operation is much higher than that required in the roasting process. The result of this operation is cuprous sulphide and a slag formed by combination of the iron oxide present with the flux. The cuprous sulphide, with some unaltered iron sulphide, temperature. When heated in air or oxygen the metal becomes black on the surface, owing to the formation of a thin layer of oxide.

With exclusion of air copper is scarcely dissolved by dilute hydrochloric or sulphuric acid; on the application of heat and in the presence of air, however, either will slowly dissolve it. Dilute nitric acid readily dissolves it in the cold. It is also dissolved by ammonia water in the presence of air.

Uses.—Metallic copper is used for making many kinds of vessels for manufacturing and domestic purposes, for sheathing ships, in the manufacture of money, in cartridge-shells, and especially in alloys.

The total production of copper in the United States for 1893 amounted to [illegible] pounds, valued at $34,677,940. This is about one-half the total production of the world.

Alloys of Copper.—The most important alloys of copper are those it forms with zinc and tin.

Brass is composed of about 70 per cent. copper and 30 per cent. zinc, with sometimes 2 or 3 per cent. of tin and 0.25 to 0.80 per cent. of lead. Brass is superior to copper because it does not tarnish so readily, it has a more pleasing color, is harder, has a lower melting point, and when cast does not blister. *Pinchbeck*, or *tombak*, is a brass containing 85 parts copper and 15 parts zinc.

The following are the percentages in some of the other important alloys of copper:

	Copper.	Tin.	Lead.
Bell metal	78	22	. .
Gun metal	90	9	. .
Art bronze	86.6	6.6	3.3

COPPER AND THE HALOGENS.

Cuprous Chloride, Cu_2Cl_2, is formed by dissolving cuprous oxide in hydrochloric acid, taking care to exclude air. It is probably most readily prepared by boiling cupric chloride with hydrochloric acid and copper turnings, with the addition of a little platinic chloride to establish galvanic action. On pouring the clear solution into water, which has been heated to expel air, cuprous chloride separates as a white, crystalline precipitate of microscopic tetrahedra.

Properties.—Cuprous chloride is a white, crystalline powder, which may be recrystallized by dissolving in hot, concentrated hydrochloric acid; it is insoluble in water, but is soluble in solution of ammonia.

On the application of heat cuprous chloride melts at 434°, and on cooling it forms a solid, crystalline mass. Near 1000° it is volatilized, and the vapor has a specific gravity of 6.93 (air = 1), indicating the formula Cu_2Cl_2.

by heating to redness copper nitrate or oxycarbonate, or by heating metallic copper to redness with access of air.

Properties.—Cupric oxide is a fine, amorphous, brownish-black powder: sometimes it is found in scales. It is insoluble in water, but easily dissolves in acids with the formation of cupric salts; it is also soluble in solution of ammonia.

When heated in the presence of hydrogen, carbon monoxide, marsh-gas, and many other organic substances, cupric oxide readily gives up its oxygen and is reduced to metallic copper. On account of this property it is much employed in organic analysis.

When fused with glass it imparts to the latter a light-green color; it is, therefore, employed in the preparation of artificial emeralds.

Cuprous Hydrate, $Cu_2(OH)_2$, having this formula, is not known, but a compound derived from it, having the composition $4Cu_2O.H_2O$, is made by pouring a solution of cuprous chloride into a cold solution of sodium hydrate. It is a bright yellow precipitate. It readily passes into cuprous oxide on the application of a gentle heat, and on exposure to air becomes blue by oxidation.

Cupric Hydrate, $Cu(OH)_2$, is readily obtained as a light-blue, bulky precipitate, when a solution of copper sulphate is treated in the cold with excess of sodium hydrate. When this mixture is boiled, the hydrate is converted into a black compound having the composition $Cu(OH)_2 \cdot 2CuO$, and this, when dried and ignited, is converted into CuO.

At least two other oxides of copper are known,—namely, Cu_4O, copper tetroxide, and copper superoxide or dioxide, $CuO_2.H_2O$.

OXYGEN SALTS OF COPPER.

Cupric Sulphate, $CuSO_4.5H_2O$. **Cupri Sulphas**, U. S. P.—This salt is most readily prepared by dissolving copper in sulphuric acid:

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

The clear solution is decanted and allowed to crystallize, and these crystals are further purified by recrystallization. Copper sulphate is a by-product in several metallurgical operations, so that its preparation is usually carried on in conjunction with them. The crude copper obtained in smelting the ores is treated with sulphuric acid, and thus converted into sulphate. Copper pyrites are roasted, when the following reaction takes place:

$$Cu_2S + 5O = CuSO_4 + CuO.$$

This mixture is then treated with so much sulphuric acid as is necessary to convert the oxide into sulphate.

Large quantities of copper sulphate are obtained in the refining of silver when that metal contains copper and gold. Silver and copper sulphates are formed, and from their solution the silver is

Copper Nitrate, $Cu(NO_3)_2.3H_2O$, *Cupric Nitrate*, is prepared by treating, in a capacious flask, 1 part of copper turnings with 11 parts of nitric acid of 25-per-cent. strength. The mixture is carefully warmed until the reaction begins, which then continues quietly without the further application of heat:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + N_2O_2 + 4H_2O.$$

The solution is diluted with water, filtered clear, and then evaporated until a film forms, when it is set aside to crystallize.

Properties.—Copper nitrate occurs in deep-blue, prismatic crystals; it possesses a sharp metallic taste, and is easily soluble in water and in alcohol. At low temperatures crystals are formed with 6 molecules of water. Like the sulphate, this salt forms an ammonia compound, having in this case the formula $Cu(NO_3)_2.4NH_3$.

Copper nitrate is used in dyeing and in calico-printing; it is also a convenient compound from which to prepare pure copper oxide.

Copper Phosphate, $Cu_3(PO_4)_2.3H_2O$, is formed when copper carbonate is dissolved in dilute phosphoric acid; on warming the solution to 70° the salt is deposited as a bluish-green, insoluble precipitate. Various compounds of copper and phosphoric acid are found in nature.

Copper Arsenite, $CuHAsO_3$, is known as *Scheele's green*, or *Swedish green*, and is obtained by mixing solutions of copper sulphate and potassium arsenite. *Paris green* is an aceto-arsenite of copper, and will be considered later.

Copper Arsenate, $Cu_3(AsO_4)_2.4H_2O$, is formed as an amorphous precipitate by warming equivalent quantities of copper nitrate and calcium arsenate with a little water to 60°. By varying the proportions of the above salts compounds of different composition may be obtained.

Copper Borate of variable composition is obtained by mixing solutions of copper sulphate and borax.

Copper Silicate, $CuSiO_3$, is found in nature with variable amounts of water. It may be obtained as a blue-green precipitate by mixing solutions of copper sulphate and sodium silicate.

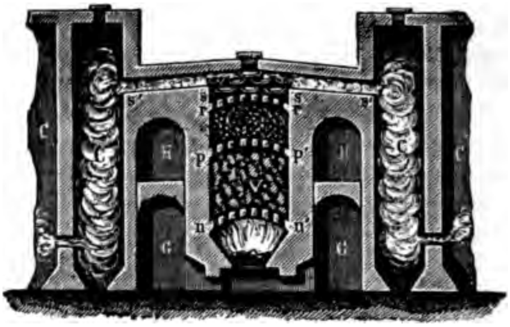
Copper Carbonate.—The normal salt, $CuCO_3$, is not known, but a compound having the composition $CuCO_3,Cu(OH)_2$, is found in nature as the mineral malachite. Azurite, $2CuCO_3,Cu(OH)_2$, occurs with malachite and other copper ores.

Malachite occurs in the Urals, at Cornwall, England, and in various parts of the United States. It is susceptible of a high polish, and is on this account much used for making vases, ornamental table tops, and jewelry.

Azurite is sometimes known as blue malachite, and is employed in the same manner as the green variety.

while at Almaden the vapors are conducted through a long series of vessels known as *aludels*, shown in Fig. 77. The combination between the mercury and sulphur is more easily destroyed in the presence of iron or lime, so that one of these is sometimes heated with the ore. When lime is employed the reaction is as follows:

FIG. 76.

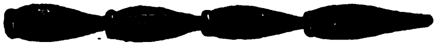


Mercury furnace.

$$4HgS + 4CaO = 4Hg + CaSO_4 + 3CaS.$$

In the United States these furnaces are usually so constructed as to be worked continuously, while in the older localities it is customary to allow the furnace to cool after each charge of about 50 tons has been heated; this is usually accomplished in one day, and then four or five days are required for the cooling before another charge can be filled in. Mercury prepared in this manner is sent into commerce in iron bottles holding about 35 kilos. It contains mechanical impurities as well as other metals like lead, silver, tin, bismuth, copper, and zinc, and must be purified by first pressing through chamois or linen, and then by distilling from iron retorts. The distillation is assisted by a Torricellian vacuum. The metallic impurities may also be removed by treatment with dilute nitric acid; this is best accomplished by running the metal into the acid in the form of a fine spray, as when it is forced through a piece of porous wood.

FIG. 77.



Aludels.

Properties.—At ordinary temperatures mercury is a liquid,

Preparation.—When hydrochloric acid or a soluble chloride is added to a solution of mercurous nitrate, calomel is precipitated. The same result may be attained by passing sulphur dioxide into a solution of mercuric chloride. The product thus obtained is not satisfactory for medicinal use, as it is crystalline and granular. The salt is, therefore, usually prepared by sublimation. This is accomplished by heating a mixture of 36 parts of sulphuric acid with 24 parts of mercury, until the latter is dissolved and a dry salt remains. The mercuric sulphate thus formed is rubbed with 24 parts of mercury until the globules disappear, and then with 18 parts of common salt. The mixture is then sublimed in such a manner as to rapidly condense the vapor and form a very fine amorphous product. This is in some cases accomplished by forcing a jet of steam into the condenser with the vapor of the calomel, and in other cases by a current of cold air in like manner. The reactions involved are as follows:

$$\underset{\text{Mercury.}}{Hg} + \underset{\text{Sulphuric Acid.}}{2H_2SO_4} = \underset{\text{Mercuric Sulphate.}}{HgSO_4} + \underset{\text{Sulphur Dioxide.}}{SO_2} + \underset{\text{Water.}}{2H_2O.}$$

$$\underset{\text{Mercuric Sulphate.}}{HgSO_4} + \underset{\text{Mercury.}}{Hg} = \underset{\text{Mercurous Sulphate.}}{Hg_2SO_4.}$$

$$\underset{\text{Mercurous Sulphate.}}{Hg_2SO_4} + \underset{\text{Sodium Chloride.}}{2NaCl} = \underset{\text{Mercurous Chloride.}}{Hg_2Cl_2} + \underset{\text{Sodium Sulphate.}}{Na_2SO_4.}$$

The same result may be obtained by using mercuric chloride instead of the sulphate, rubbing it with an equivalent quantity of mercury and subliming.

In both cases the product is washed well with warm water to remove mercuric chloride, since the latter is soluble in that liquid. The washing is known to be complete when ammonia causes no further turbidity with the wash-water.

Properties.—Calomel is "a white, impalpable powder, becoming yellowish-white on being triturated with strong pressure, and showing only small, isolated crystals under a magnifying power of one hundred diameters. It is odorless and tasteless, and permanent in the air." It is "insoluble in water, alcohol, or ether, and also cold dilute acids."

On the application of heat calomel is volatilized without melting. One of its most characteristic reactions is that of blackening on the addition of lime water or solution of ammonia. Whe concentrated hydrochloric acid is boiled with calomel, the latte is converted into mercuric chloride and mercury. Hot nitric aci converts it into mercuric chloride and nitrate, and hot sulphuric acid also decomposes it, with evolution of sulphur dioxide and formation of mercuric chloride and sulphate.

Uses.—The chief use of calomel is in medicine.

Mercuric Chloride, $HgCl_2$, *Corrosive Sublimate.* **Hydrargyri Chloridum Corrosivum,** U. S. P.—This salt was described by Geber in the eighth century. It may be prepared in a small way by dissolving with the aid of heat 10 parts of mercuric oxide in 14 parts of 25-per-cent. hydrochloric acid, previously diluted with 28 parts of water:

$$HgO + 2HCl = HgCl_2 + H_2O.$$

The method usually employed on a large scale consists in heating 4 parts of mercury and 5 parts of sulphuric acid, with formation of mercuric sulphate:

$$Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O.$$

The dried mercuric sulphate is intimately mixed with half its weight of common salt and a little manganese dioxide to prevent formation of mercurous salts.

The dry mixture is placed in glass vessels; these are half buried in sand and heated until the mercuric chloride is sublimed into the upper half; the vessels are then broken, and the salt renewed. The reaction which takes place in the sublimation is as follows:

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$

Properties.—Sublimed corrosive sublimate forms white, opaque, or translucent, crystalline masses, odorless, and having a sharp, metallic taste. It is permanent in the air. When rubbed in a mortar it yields a pure white powder; calomel becomes yellow when so treated.

Corrosive sublimate is soluble in 16 parts of water at 15°, and in 2 parts of boiling water; in 3 parts of cold and in 1.2 parts of boiling alcohol; it is also dissolved by 4 parts of ether, and by 14 parts of glycerin.

On the application of heat the salt fuses at 265° to a colorless liquid, which at about 300° volatilizes in dense white vapors, leaving no residue. "The aqueous solution reddens litmus paper, but becomes neutral on the addition of sodium chloride." The solution in water slowly decomposes when exposed to the light, as follows:

$$2HgCl_2 + H_2O = Hg_2Cl_2 + 2HCl + O.$$

The hot acids dissolve mercuric chloride without decomposing it; this is best illustrated by the salt's subliming unchanged from its solution in concentrated sulphuric acid.

Mercuric chloride forms a number of basic chlorides; for instance when the aqueous solution is boiled with mercuric oxide and the solution is cooled to 60°, a number of basic chlorides separate, and the clear solution poured off from these yields, on further cooling, a compound having the composition $2HgCl_2.3HgO$. When equal volumes of cold, saturated solutions of corrosive sublimate and acid potassium carbonate are mixed a compound having the composition $HgCl_2.3HgO$ separates in golden yellow scales.

Mercuric chloride forms a large number of double chlorides with the alkali metals; these double chlorides are more soluble than the mercuric salt. When a watery solution containing equal weights of mercuric chloride and ammonium chloride is evaporated a residue is obtained which was formerly known as *sal alembroth*, and has the composition $2NH_4Cl,HgCl_2.H_2O$. This is a powerful antiseptic, not so irritating as the mercuric salt alone.

Uses.—Mercuric chloride is a valuable agent from which to prepare the other salts of mercury. It also has extended use in medicine, especially as an antiseptic. Internally it acts as a powerful poison, except in very small doses. The best antidote is raw white of egg.

Mercurous Bromide, Hg_2Br_2, may be prepared by adding hydrobromic acid or sodium bromide to solution of mercurous nitrate; in this form it bears a close resemblance to calomel.

Mercuric Bromide, $HgBr_2$, is obtained by treating mercury under water with an excess of bromine; it crystallizes from water in glistening scales, and from alcohol in rhombic needles. It is not so soluble in water as the chloride, but is easily soluble in alcohol and in ether.

Mercurous Iodide, Hg_2I_2. **Hydrargyri Iodidum Flavum**, U. S. P.—This form of mercurous iodide has replaced the green variety which was official in the earlier Pharmacopœias, and which was prepared by rubbing in a mortar 40 parts of mercury with 2 to 3 parts of alcohol and 25.5 parts of iodine added in small portions at a time. The present official process which yields the yellow iodide consists in precipitating a solution of mercurous nitrate with one of potassium iodide:

$$Hg_2(NO_3)_2 + 2KI = Hg_2I_2 + 2KNO_3.$$

The precipitate is directed to be washed with alcohol to remove the last traces of mercuric salt, and to be kept in dark amber-colored vials, with the least possible exposure to light.

Properties.—The official salt is "a bright yellow, amorphous powder, odorless and tasteless. By exposure to light it becomes darker, in proportion as it undergoes decomposition into metallic mercury and mercuric iodide." The green mercurous iodide owes its color to the admixture with it of metallic mercury and, perhaps, some mercuric iodide.

Mercurous iodide is nearly insoluble in water, and entirely insoluble in alcohol or ether.

On the careful application of heat to 290° the salt melts to a black liquid, and then sublimes in yellow crystals. The sublimation begins as low as 120°.

Mercuric Iodide, HgI_2. **Hydrargyri Iodidum Rubrum, U. S. P.**—This salt is prepared by taking mercuric chloride, 40 parts, potassium iodide, 50 parts, each in a sufficient quantity of water, and pouring the two solutions simultaneously and in a thin stream, with active stirring, into 2000 parts of distilled water:

$$HgCl_2 + 2KI = HgI_2 + 2KCl.$$

The precipitate is well washed, dried in the dark between folds of filter paper at a temperature not exceeding 40°. The product should be kept excluded from the light. Mercuric iodide may also be prepared by rubbing in a mortar 20 parts of mercury, moistened with 2 or 3 parts of alcohol, and 25.5 parts of iodine, until a uniform product is obtained.

Properties.—Mercuric iodide is a scarlet-red, amorphous powder, without odor or taste. It is almost insoluble in water; soluble in 130 parts of alcohol at 15°, and in 15 parts of boiling alcohol. Since the salt is soluble in solution of potassium iodide and solution of mercuric chloride, it is important in its preparation that the proportion of these two salts be properly adjusted.

On the careful application of heat the salt melts at 238° to a dark-yellow liquid. It slowly sublimes without decomposition, forming yellow, rhombic crystals, which after some time become red.

Mercuric iodide readily forms double salts with the iodides; for instance, from its hot, saturated solution in potassium iodide there separates first mercuric iodide, and then by further cooling or evaporation a double salt having the composition $HgI_2,KI.1\frac{1}{2}H_2O$, in yellow prisms. This compound, under the name of *Mayer's solution*, is a useful alkaloidal reagent. A similar compound with ammonium iodide is known.

Mercurous Fluoride, Hg_2F_2, is formed by digesting calomel with silver fluoride; it forms in small, yellow crystals, soluble in water.

Mercuric Fluoride, $HgF_2.2H_2O$, forms as a white, crystalli
when mercuric chloride is treated with an excess of hydrofluoric

MERCURY AND OXYGEN.

Mercurous Oxide, Hg_2O, is obtained by precipitatin
curous nitrate with sodium or potassium hydrate. The p
is an odorless and tasteless brownish-black powder, insol
water, and readily decomposed into mercuric oxide and me

Mercuric Oxide, HgO.—The Pharmacopœia recogniz
varieties of mercuric oxide, the yellow, **Hydrargyri Ox
Flavum**, and the red, **Hydrargyri Oxidum Rubrum.**
yellow variety is prepared by pouring a solution of 100 gra
of mercuric chloride in 1000 cubic centimeters of water i
solution of 40 grammes of sodium hydrate (90-per-cent. stre
in 1000 cubic centimeters of water :

$$HgCl_2 + 2NaOH = HgO + 2NaCl + H_2O.$$

The precipitate is well washed, and dried at a temper
below 30° without exposure to light.

The red mercuric oxide, or *red precipitate*, is prepared b
solving 10 parts of mercury in 30 parts of nitric acid (2
cent.), evaporating to dryness, and then heating on a
bath so long as yellowish vapors escape. The product obt
by the above proportions of mercury and nitric acid is a
mercuric nitrate. On the commercial scale this basic s
rubbed with 10 parts of mercury until the particles of the
cease to be visible; the result is a basic mercurous nitrate w
on heating, yields mercuric oxide.

Properties.—The yellow oxide is officially described a
light orange-yellow, amorphous, heavy, impalpable pow
while the red oxide is stated to consist of "heavy, orange
crystalline scales, or a crystalline powder, becoming more y
the finer it is divided." Both varieties are odorless, with a
[illegible] permanent in the air. The yellow oxide dar
[illegible] light. Both are almost insoluble in water, in
[illegible] but readily and completely soluble in dilute h
[illegible] forming colorless solutions. On the a
[illegible] oxides become darker in color, the y
[illegible] color, and at a low red heat they are
[illegible] into oxygen and mercury.

[illegible] The oxides of mercury are used in the prepar
[illegible] salts, and in medicine for external
[illegible]

OXYGEN SALTS OF MERCURY.

Mercurous Chlorate, $Hg_2(ClO_3)_2$, is formed when mercurous oxide is dissolved in chloric acid, and the solution evaporated at ordinary temperatures over sulphuric acid. It is deposited in rhombic prisms which decompose at 250°, and when heated with organic matter deflagrate violently.

Mercuric Chlorate, $Hg(ClO_3)_2.H_2O$. —This salt is obtained by dissolving mercuric oxide in warm chloric acid. It crystallizes on cooling in small, rhombic pyramids.

Mercurous Sulphate, Hg_2SO_4, is prepared by heating concentrated sulphuric acid with an excess of mercury. It is a dark, crystalline powder, which melts when heated and solidifies on cooling into a crystalline mass.

Mercuric Sulphate, $HgSO_4$.—This salt is obtained as a white, crystalline mass by heating mercury with an excess of sulphuric acid. The solution in sulphuric acid is assisted by the addition of nitric acid. When gently warmed mercuric sulphate becomes yellow, then red, and at a stronger heat is decomposed into mercury, oxygen, sulphur dioxide, and mercurous sulphate. When mercuric sulphate is thrown into water it is decomposed into the basic salt.

Hydrargyri Subsulphas Flavus, U. S. P., or *Turpeth Mineral.* — This official salt is prepared by dissolving 100 grammes of mercury in a mixture of 30 cubic centimeters of sulphuric acid and 25 cubic centimeters of nitric acid. and, after drying and powdering the resulting mercuric sulphate, stirring it into 2 litres of distilled water. Basic mercuric sulphate has the composition $Hg(HgO)_2SO_4$. It is "a heavy, lemon-yellow powder, odorless, and almost tasteless; permanent in the air. Soluble in 2000 parts of water at 15°, and in 600 parts of boiling water; insoluble in alcohol; readily soluble in nitric or hydrochloric acid." On the application of heat the salt turns red, becoming yellow again on cooling. At higher temperatures it is decomposed and volatilized without leaving any residue.

Uses.—Turpeth mineral is employed in small doses as an alterative, and in larger doses as an emetic, although its use is not without some danger.

Mercurous Nitrate, $Hg_2(NO_3)_2.2H_2O$, is prepared by acting on mercury in the cold with dilute nitric acid. One part of mercury is covered in a beaker with 1.5 parts of nitric acid (25 per cent.) and set aside in a cool place for several days:

$$6Hg + 8HNO_3 + 2H_2O = 3Hg_2(NO_3)_2.2H_2O + 2NO.$$

The solution is allowed to evaporate until crystals form, when it is warmed and filtered through asbestos from the undissolved mercury. The filtrate yields the pure crystals on cooling.

Properties.—The white or colorless salt readily loses its water of crystallization. It is soluble in warm water, yielding an acid solution. In the presence of much water it is partly decomposed into a basic salt of variable composition.

Uses.—Mercurous nitrate has some use in the laboratory as a reagent, and especially for the detection of protein substances under the microscope. When used in this way it is known as *Millon's reagent*, and is prepared by dissolving 1 part of mercury in 1 part of cooled, concentrated nitric acid, and adding 2 parts of distilled water.

Mercuric Nitrate, $Hg(NO_3)_2$.—This salt is official in solution as **Liquor Hydrargyri Nitratis.** It is made by dissolving 40 grammes of red mercuric oxide in a mixture of 45 grammes of nitric acid and 15 grammes of distilled water. This solution has a specific gravity of 2.1, and contains 60 per cent. of the salt. When this solution is concentrated at ordinary temperatures over sulphuric acid it deposits deliquescent crystals, having the composition $2Hg(NO_3)_2.H_2O$. Basic salts of mercuric nitrate are readily formed.

The solution of mercuric nitrate when mixed with fat, or lard oil, forms an important official ointment, under the name of **Unguentum Hydrargyri Nitratis.**

Mercurous Phosphate, $Hg_6(PO_4)_2$, is a white, amorphous, insoluble precipitate, formed by precipitating mercurous nitrate in solution by a solution of sodium phosphate.

Mercuric Phosphate, $Hg_3(PO_4)_2$, is formed when solution of sodium phosphate is added in excess to solution of mercuric nitrate. It is a white precipitate, insoluble in water, but soluble in acids.

Mercurous Carbonate, Hg_2CO_3, exists as a light-yellow, easily decomposed powder; insoluble in water. It is prepared by precipitating mercurous nitrate with excess of potassium bicarbonate. Light must be excluded.

Mercuric Carbonate.—This compound is known only in the form of basic salts. One of these has the formula $HgCO_3.2HgO$, another $HgCO_3.3HgO$. The former is produced when potassium bicarbonate is added to solution of mercuric nitrate; the latter is formed when neutral potassium carbonate is added to solution of mercuric nitrate; both are brownish-red precipitates.

Mercuric Cyanide, $Hg(CN)_2$, is prepared by dissolving mercuric oxide in hydrocyanic acid, or by boiling 1 part of potassium ferrocyanide with 2 parts of mercuric sulphate and 8 parts of water. It is soluble in 8 parts of water, and may be crystallized from hot, aqueous solution in needles. It readily forms double salts. Formerly it was official, and had some use in medicine in place of mercuric chloride.

Mercuric Cyanate, $Hg(OCN)_2$, is obtained as a white, crystalline precipitate by adding a solution of potassium cyanate to one of mercuric chloride.

Mercuric Thiocyanate, $Hg(SCN)_2$, is prepared by precipitating a mercuric salt with potassium thiocyanate. This compound is used in the preparation of the so-called Pharaoh's serpents. The powder is made into a plastic mass with gum and water, and then formed into cones or cylinders. These, when once ignited, burn with a bluish flame and yield a bulky ash, which takes somewhat the appearance of a serpent.

MERCURY AND SULPHUR.

Mercuric Sulphide, HgS.—This compound is found in two forms, according to its method of preparation. The amorphous, black variety is produced by precipitating mercuric salts with hydrogen sulphide. The crystalline, red variety is formed by sublimation of the black compound. The red is also found in nature as *cinnabar*. It occurs in red, hexagonal prisms or in crystalline masses. The black variety was formerly known as *Ethiops mineral*.

Vermilion is a very finely-divided red sulphide prepared, usually, by subliming a mixture of 8 parts of sulphur and 42 parts of mercury.

Uses.—Mercuric sulphide was formerly used in medicine, but at the present time it is rarely employed in that way. Vermilion and cinnabar are much used in paints.

MERCURY AMMONIUM COMPOUNDS.

Mercurous Ammonium Chloride, $(NH_3)_2Hg_2Cl_2$.—When calomel is subjected to the action of dry ammonia a black compound of the above composition is formed. It is readily decomposed on heating, or by exposure to the air.

Dimercurous Ammonium Chloride, NH_2Hg_2Cl.—This compound is formed when calomel is treated with aqueous ammonia.

When mercurous nitrate is used instead of the chloride, a compound of somewhat variable composition is formed, having, presumably, the formula $NH_2Hg_2NO_3$. It was the *mercurius solubilis Hahnemanni*. It is readily decomposed on exposure to light.

Mercuric Ammonium Chloride, NH_2HgCl. **Hydrargyrum Ammoniatum,** U. S. P. *White Precipitate.*—This compound is prepared by pouring a solution of 100 grammes of mercuric chloride in 2000 cubic centimeters of warm water, into 150 cubic centimeters of ammonia water (10 per cent.), keeping the latter in excess.

$$HgCl_2 + 2NH_4OH = NH_2HgCl + NH_4Cl + 2H_2O.$$

The precipitate is collected, washed well, and dried between the folds of bibulous paper at a temperature not exceeding 30°. Light should be excluded as much as possible during the process.

Properties.—White precipitate occurs in "white, pulverulent pieces, or a white, amorphous powder, without odor, and having an earthy, afterwards styptic and metallic taste. Permanent in the air." It is insoluble in water and in alcohol. By prolonged washing it is converted into a basic compound and becomes yellowish in color.

Warm hydrochloric, nitric, or acetic acid readily dissolves it. The salt is readily soluble in cold solution of ammonium carbonate, and in warm solution of sodium hyposulphite.

On the application of heat white precipitate is decomposed without fusion, and below redness it is completely volatilized. When heated with solution of potassium or sodium hydrate the salt turns yellow and evolves ammonia.

Uses.—White precipitate is a valuable remedy for external application.

Other compounds of mercuric ammonium chloride are known. The most important is the *Mercuric Diammonium Chloride*, $(NH_3)_2HgCl_2$, also known as *fusible white precipitate*. It may be obtained by adding 20 parts of yellow mercuric oxide to a boiling solution of 100 parts of ammonium chloride in 350 parts of water. On cooling, crystals of the above composition separate. Towards solvents this compound behaves similarly to the preceding one, but on the application of heat it readily fuses with evolution of nitrogen and ammonia.

CHAPTER VI.

ALUMINUM AND THE RARE EARTHS.

ALUMINUM.

Symbol, Al. *Atomic Weight*, 27.04. *Valence*, III or $(Al_2)^{VI}$.

History.—Alumina, the oxide of the metal, has long been known. It was formerly regarded as identical with lime: it was shown to be distinct from that substance by Marggraff in 1754. The metal was first obtained by Wöhler in 1828 by the reduction of the chloride by sodium.

Occurrence.—The most abundant sources of aluminum are the oxide and its hydrates and the silicates. The oxide is found native as corundum, of which the fine crystallized varieties constitute the gems sapphire and ruby, while the granular variety is known as emery. Of the hydrates, the monohydrate, $Al_2O_2(OH)_2$, is the mineral diaspore, the dihydrate, $Al_2O(OH)_4$, is found admixed with ferric oxide in bauxite, and the trihydrate, $Al_2(OH)_6$, as the mineral gibbsite. Of these the second is by far the most important, and is now mined both in France and in this country in Georgia and Alabama as the chief material for the preparation of alumina in the production of the metal and for the manufacture of alum. A double fluoride of aluminum and sodium is also found in Greenland as the mineral cryolite; a basic sulphate is found as alunite; and lastly numerous silicates are found in the various clays, of which kaolin or porcelain clay is the purest.

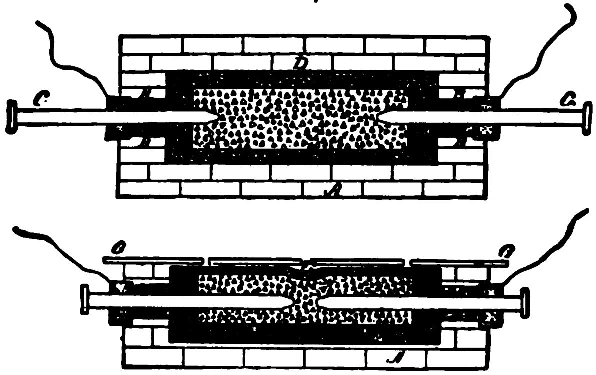
Preparation.—The first working process for the manufacture of aluminum is due to Deville, who developed and improved Wöhler's method, using the double chloride of aluminum and sodium, which he caused to react with metallic sodium, according to the reaction:

$$Al_2Cl_6.6NaCl + 6Na = Al_2 + 12NaCl.$$

This process, elaborated in 1855, remained the sole one for its manufacture for thirty years. It was an expensive method, however, in that it involved the use of the costly metal sodium and because the reaction was not capable of being made a continuous one. After the double chloride had been prepared by the action of chlorine upon a mixture of alumina, charcoal, and common salt, it was mixed with some powdered cryolite (double fluoride of sodium and aluminum) to give fusibility to the slag, and placed in shallow trays with chips of metallic sodium. This mixture was then placed on the hearth of a reverberatory furnace previously heated to redness and the doors closed, when an energetic reaction took place. After several hours' heating the slag was run out and the melted aluminum drawn off into ingot moulds. With the advent of cheaper sodium as made by the Castner process (see p. 317) the price of aluminum as made by the Deville process was greatly reduced, but it finally was given up because of the introduction of the electrolytic methods.

In 1885 the Cowles Bros.' patent for the reduction of alumina (in the form of corundum) by carbon at the temperature of the electric arc was made public. This process is not so much adapted for the production of pure aluminum as for the formation of aluminum alloys, as aluminum bronzes (copper and aluminum). For this purpose copper is added to the mixture of broken corundum and coke, which is packed in the charcoal-lined boxes shown in Fig. 78, which shows the Cowles furnace in plan and in longitudinal section. The heavy carbon electrodes, delivering the current from a powerful dynamo, are introduced into this mixture from the side, and can be moved so as to change the distance apart as the reduction proceeds and the conductivity of the mass changes. The alloy first obtained will contain from 15 to 30 per cent. of aluminum. This is then reduced by remelting with copper, so that alloys of from 5 to 10 per cent. of aluminum are produced, in which form they are sold. Two purely electro-

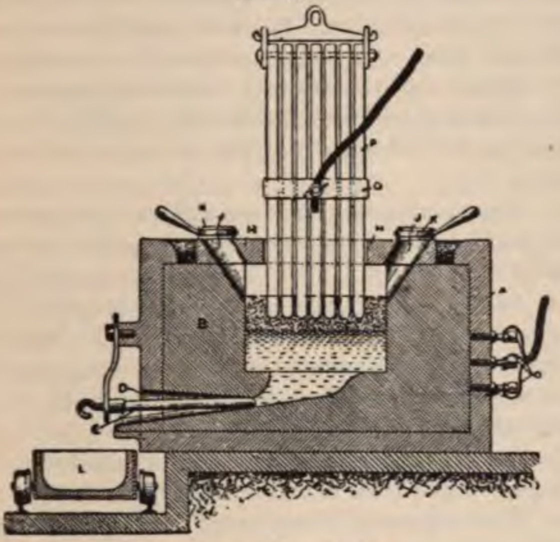
FIG. 78.



Cowles' aluminum furnace.

lytic processes have since been introduced,—the Heroult process in 1887 and that of Hall in 1889, and these now practically monopolize the manufacture of the pure metal. The former, as improved and carried out on a large scale at Neuhausen on the Rhine, in Switzerland, is illustrated in Fig. 79. The positive electrode here is a bundle of carbon plates, and is suspended in the molten bath, while the negative electrode is of metal, and is introduced from below, where the metal may also be drawn off. The material to be electrolyzed is a mixture of cryolite and alumina. These works now produce daily 5000 lbs. of an aluminum of 98–99 per cent. The Hall process, as worked by the Pittsburg Reduction Co., electrolyzes a bath of a double fluoride of aluminum and sodium, to which alumina is added, from time to time, to regenerate the bath and re-form the fluoride decomposed. The metal made by this process is very pure, running over 99 per cent. The Pittsburg Reduction Co., in their new plant just finished at Niagara Falls, have a capacity of 8000 lbs. per day. The total production of aluminum in the United States in 1893 was 312,000 lbs. In 1892 there was made by the Heroult process in Switzerland 286,100 kilos, and in France 60,000 kilos.

FIG. 79.



Heroult process for aluminum.

Properties.—Aluminum is a bluish-white metal of high lustre, and a specific gravity of 2.56 when cast, and 2.74 when drawn into wire. It is a little softer than silver, but its ductility allows it to be drawn, punched, or spun into almost any form. It fuses at 625°, being intermediate between zinc and silver. It is practically non-tarnishable in the air, either dry or moist, and hydrogen sulphide has no action upon it. It is not acted upon by water at any temperature. Sulphuric acid does not attack it, nitric acid only slowly at a boiling temperature, but hydrochloric acid, both dilute and concentrated, dissolves it rapidly. Solutions of the alkaline hydrates also attack it rapidly, dissolving it with evolution of hydrogen and the formation of an alkaline aluminate.

Uses.—Aluminum is used in large and increasing amounts for fancy and useful articles because of the two qualities of lightness and freedom from tarnish. It is peculiarly adapted for culinary vessels, as the effect of vegetable juices and acids upon it has been shown to be less than upon tin and copper. The alloys of aluminum, however, from a commercial point of view, form its most important applications. Of these, first in importance are the alloys with copper, known as aluminum bronzes, and composed of 90–95 per cent. copper and 5–10 per cent. aluminum. These alloys are superior to brass in tensile strength, and afford superior castings. The addition of a very small amount of aluminum to other metals seems, in many cases, to allow of superior castings being made. Thus, from 0.02 to 0.04 per cent. of aluminum added to steel greatly improves it; 0.01 per cent. of aluminum added to zinc makes the molten metal thinner, and reduces the amount of oxidation that takes place in the galvanizing process; zinc with 0.05 per cent. of aluminum is also used for desilverizing bullion. The aluminum scale beams now made, which combine rigidity with lightness, contain 3 per cent. of silver and 2 per cent. of copper.

ALUMINUM AND THE HALOGENS.

Aluminum Chloride, Al_2Cl_6 or $AlCl_3$.—The determination of vapor-density shows that the chloride has the molecular weight corresponding to the former of these formulas. Hence we must assume that in this, and probably the other aluminum compounds, aluminum acts as a double atom with the valence six. The chloride is obtained by the action of chlorine at a red heat upon a mixture of alumina and carbon. Clay may be used instead of alumina, but bauxite is almost universally employed, and from it alumina is prepared. Aluminum chloride is obtained in this way by sublimation in white hexagonal leaflets. It is very deliquescent, and rapidly absorbs moisture from the air. It crysstallizes from concentrated hydrochloric acid solution with 6 molecules of water. The aqueous solution cannot be evaporated to dryness without decomposition into alumina and hydrochloric acid. It readily forms double chlorides with the alkaline chlorides, and the double aluminum and sodium chloride is used in the Deville process for preparing the metal. A weak solution of aluminum chloride is believed to possess disinfecting value, and is used in admixture with other chlorides for this purpose.

Aluminum Bromide, Al_2Br_6, is obtained by a method analogous to that described for the chloride, and has analogous properties.

Aluminum Iodide, Al_2I_6, is best obtained by the direct action of iodine upon aluminum. It is a white, crystalline mass, fusing at 185°, and boiling at about 400°.

Aluminum Fluoride, Al_2F_6, is formed by passing hydrogen fluoride over heated alumina, or by the reaction of aluminum sulphate and fluorspar, as now carried out on a large scale in the Grabau process for making metallic aluminum. The aluminum fluoride may then be electrolyzed, or heated with a mixture of sodium carbonate and charcoal, and the metal obtained by reduction. A double fluoride of aluminum and sodium, occurring native in Greenland as *cryolite*, is still more important in the aluminum industry. Cryolite is also the raw material for the manufacture of sodium carbonate (see p. 345) and of alum.

ALUMINUM AND OXYGEN.

Aluminum Oxide (Alumina), Al_2O_3, is found native as corundum, ruby and sapphire, and emery. Obtained artificially by igniting the hydrate, it forms a white, amorphous powder, which is insoluble in water, and fuses only at the highest temperature. Commercially it is now prepared from bauxite, either by the action of sulphuric acid or of sodium carbonate, the former process dissolving out the alumina from the impurities, and the latter making a sodium aluminate, which is soluble.

The Solvay Process Co., of Syracuse, N. Y., have recently completed a plant for making alumina from bauxite, the capacity of which is 20 tons per day.

Aluminum Hydrate, $Al_2(OH)_6$ (**Alumini Hydras,** U. S. P.), is prepared by the action of ammonium hydrate or an alkali carbonate upon a soluble aluminum salt. The official process uses sodium carbonate and alum solutions, and then strains off the precipitate, and washes it thoroughly with hot water to remove the alkali sulphates. When freshly precipitated it is a white, gelatinous precipitate. When dried at a temperature not exceeding 40° it can be reduced to a uniformly fine white powder, which is insoluble in water or alcohol, but completely soluble in hydrochloric or sulphuric acid, and also in potassium or sodium hydrate solutions.

Gelatinous aluminum hydrate possesses the property of precipitating many dyestuffs from their solutions, forming insoluble colored compounds (*lakes*) with them. Hence the importance of aluminum compounds as mordants in dyeing. The acetate of aluminum is often used in this connection, as when the mordanted goods are steamed the acetic acid passes off, leaving the aluminum hydrate upon the fibre.

Aluminum hydrate in the presence of more electro-positive oxides can act as a weak acid and form salts called ***aluminates***. Of these sodium aluminate, $Al_2(ONa)_6$, is the best known, playing an important part in the "cryolite process" for making sodium carbonate (see p. 345). Similar aluminates occur in nature as minerals, as *spinel*, or magnesium aluminate, $\begin{matrix}AlO.O\\AlO.O\end{matrix}{>}Mg$, *chrysoberyl*, or beryllium aluminate, and ***gahnite***, or zinc aluminate.

OXYGEN SALTS OF ALUMINUM.

Aluminum Sulphate, $Al_2(SO_4)_3+16H_2O$ (**Alumini Sulphas**, U. S. P.).—This salt, with 16 molecules of water of crystallization, forms a white, crystalline powder, without odor, having a sweetish, and afterwards astringent, taste. It is readily soluble in water, but insoluble in alcohol. The salt has an acid reaction on litmus paper. A commercial sulphate containing $18H_2O$ is also manufactured on a large scale under the name of "concentrated alum," or "alum cake." A basic sulphate, $Al_2(SO_4)_3.3Al_2O_3.9H_2O$, is found native as the mineral alunite.

Aluminum sulphate unites with alkali sulphates to form a class of well characterized and crystallizable double sulphates, which are known by the general name of ***Alums***. In a still wider sense, the term is applied to the whole class of double sulphates, in which we have a sesquisulphate, an alkali sulphate, and 24 molecules of water crystallizing together.

Aluminum and Potassium Sulphate (Potash Alum), $Al_2K_2(SO_4)_4 + 24H_2O$ (**Alumen, U. S. P.**), is manufactured on a large scale either from alum shale, bauxite, or cryolite. The first of these materials, which was generally used until recently, is a clay containing iron pyrites, which, on calcination, furnishes the sulphuric acid to combine with the alumina of the clay. The solution obtained by lixiviation of these heaps is concentrated and potassium chloride is added, when, on standing, the potash alum will crystallize out.

Alum forms large, colorless, octohedral crystals, having a sweetish but strongly astringent taste. On exposure to the air the crystals are liable to absorb ammonia and acquire a whitish coating. It is soluble in water, but insoluble in alcohol. When heated carefully to 200° it loses all its water of crystallization and leaves *dried alum* (**Alumen Exsiccatum,** U. S. P.), which retains all the chemical characters of the crystallized alum. The total production of alum in the United States in 1893 was between 45,000 and 55,000 tons.

Aluminum and Ammonium Sulphate (Ammonia Alum), $Al_2(NH_4)_2(SO_4)_4.24H_2O$, crystallizes in the same octohedral forms as potash alum, and is very similar in characters, but is slightly more soluble in water.

Sodium, rubidium, cæsium, silver, and thallium alums have all been prepared.

Aluminum Phosphate, $Al_2(PO_4)_2$, may be obtained by adding a solution of alum to sodium orthophosphate. The mineral *wavellite* is a basic aluminum phosphate, $2Al_2(PO_4)_2.Al_2(OH)_6.9H_2O$, occurring in rhombic crystals. Turquoise found in Persia, Silesia, and Mexico has the composition $Al_2(PO_4)_2.Al_2(OH)_6.2H_2O$.

Aluminum Silicates.—A large number of silicates found native are double silicates of aluminum and other bases. By the decomposition of these *in situ* pure aluminum silicates are often formed. Thus, one of the most abundant minerals is feldspar, a double silicate of aluminum and potassium or sodium. Its gradual decomposition with the elimination of the alkali gives rise to the large deposits of kaolin or porcelain clay, a very pure aluminum silicate. The common clays found so abundantly have resulted either from similar decomposition of aluminum silicate minerals or from their gradual comminution and deposit by aqueous agency.

Pottery and Ceramics.—The most important utilization of the clays is in the manufacture of the various grades of pottery and earthenware. We may distinguish between the *infusible* clays, of which kaolin or

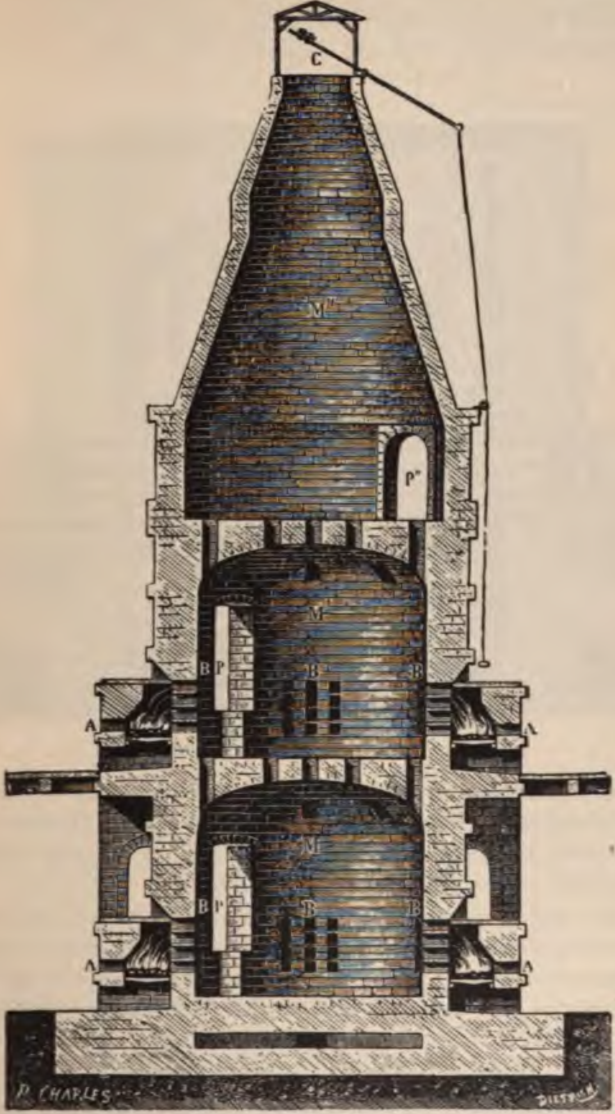
"China clay" is an example, and *fusible* clays, of which the common clays for earthenware manufacture afford examples. To these may be added the colored clays used for the brick and terra-cotta industry. The difference in chemical character of these three groups may be seen from the subjoined analyses:

	Kaolin.	Fusible Clay.	Brickmaker's Clay.
Silica	46.31 per cent.	66.38	49.44
Alumina	39.91 " "	26.08	34.26
Magnesia	0.44 " "	trace	1.94
Lime	0.43 " "	0.84	1.48
Ferrous oxide	0.27 " "	1.26	7.74
Water	12.69 " "	5.14	5.14
	100.05	99.70	100.00

From kaolin, to which has been added a so-called flux, usually feldspar, is made porcelain. The materials are thoroughly admixed in a finely-ground and levigated condition with the aid of water, and after the articles are shaped on the potter's wheel or by hand they are dried and burned in the pottery kiln. This is shown in sectional view in Fig. 80. The ware is placed in vessels known as "saggers," which are arranged one above the other in columns in the compartments of the kiln as shown in Fig. 81. The baked ware is known as "porcelain biscuit," and is then to be given a glaze. This is a mixture of silicate of alumina and alkalies, and is applied in a thin cream, dried on, and then burned again in the kiln at a temperature sufficient to cause uniform fusion on the surface.

Cements.—The natural calcareous clays and artificial mixtures of similar composition are used in the manufacture of hydraulic mortars or cements. Common or Roman cements are prepared by burning natural calcareous clays or cement-rock at a temperature short of that required to cause the sintering of the mass. Portland cement, on the other hand, is made from mixtures of limestone and clay or natural cement-rock, of such composition that when burned the product will contain from 55 to 60 per cent. of lime, from 22 to 25 per cent. of silica, and some 7 per cent. [illegible] This variety is also burned until the mass is sintered. [illegible] It is then ground, allowed several months to season, and packed in barrels. These cements are essentially basic [illegible] and alumina, and they "set" by virtue of their [illegible] and combining with water. The production of hydraulic cement in the United States for the year [illegible] 503,385 bbls. of 300 lbs., and of Portland [illegible] the same year to 596,531 bbls.

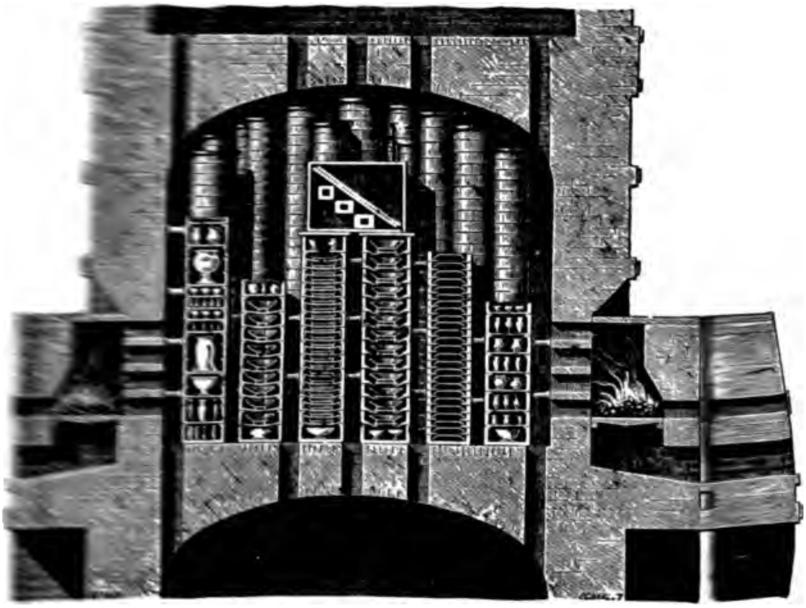
FIG. 80.



Pottery kiln, sectional view.

Ultramarine is a blue coloring matter, consisting of silica, alumina, soda, and sulphur, first found in the rare and costly mineral *lapis lazuli*, but since 1828 made artificially. A mixture of kaolin, charcoal, and sodium sulphate or carbonate is heated [illegible] clay crucibles, and the green mass thus [illegible] powder and then roasted in thin layers with [illegible] until the required blue shade is obtained.

FIG. 81.



Interior of pottery kiln filled.

Part of the sodium in ultramarine is combined as a double silicate with alumina, and part is present as sulphide. Hence, when ultramarine is heated with hydrochloric acid, hydrogen sulphide is evolved and the blue color is destroyed.

Violet and red ultramarines are also prepared at present by conducting dry hydrochloric acid gas and air over common ultramarine at 100°–150°. The present annual production of ultramarine is about 9000 tons, of which Germany produces 6500 tons.

RARE EARTHS AND METALS.

In some relatively rare minerals, like cerite, gadolinite, allanite, monazite, and samarskite, occur a number of metals, the oxides of which are very analogous to alumina in chemical characters. They will be briefly enumerated, and their relationships in the list of elements pointed out.

Scandium (Sc = 43.97) is contained in euxenite and gadolinite. Its oxide, Sc_2O_3, is a white, infusible powder like magnesia. It forms a hydrate, $Sc_2(OH)_6$, and a double sulphate or alum, $Sc_2(SO_4)_3 + 3K_2SO_4$.

It is interesting as having been discovered since the announcement of the periodic-system theory, and as filling a place pointed out in that system.

Yttrium (Yt = 88.9) is mostly obtained from gadolinite. It forms a potassium double sulphate, soluble in potassium sulphate solution, and thus separable from cerium, lanthanum, and didymium.

Lanthanum (La = 138.2) has been obtained by the electrolysis of its chloride as a metal resembling iron as regards color and lustre, and with a specific gravity 6.16.

Ytterbium (Yb = 172.6) is obtained from the so-called erbium earths by fractional decomposition of the mixed nitrates by heating. Its oxide, Yb_2O_3, is a white, infusible powder, of specific gravity 9.17.

These four elements form a sub-group of basic elements, attaching to aluminum in the third group of the periodic system (see p. 286).

Cerium (Ce = 139.9) occurs in cerite to the amount of 60 per cent. of the oxide. The metal has been obtained by the electrolysis of the chloride. It is very similar to lanthanum, but burns more readily. Its specific gravity is 6.72. It forms two oxides, Ce_2O_3 and CeO_2. The salts of the sesquioxide are colorless, while those obtained from the dioxide are yellow or brown.

Cerium Oxalate, $Ce_2(C_2O_4)_3.9H_2O$ (**Cerii Oxalas, U. S. P.**), "forms a white, granular powder, without odor or taste, and permanent in the air. Insoluble in water, alcohol, ether, or in solutions of potassium or sodium hydrate; soluble in diluted sulphuric or hydrochloric acid. When heated to redness it is decomposed, leaving a residue of reddish-yellow ceric oxide." Cerium nitrate has also been employed in medicine, although not official. The cerium salts are nervine tonics, and useful in cases of vomiting and dyspepsia.

Didymium (Di = 142) forms two oxides, Di_2O_3 and Di_2O_5. The salts of didymium by fractional crystallization can be broken up into salts of what are apparently two distinct bases, *neo-didymium* and *praseo-didymium;* the salts of the first class are rose-red and of the second yellowish-green in color.

Samarium (Sm = 149.62) was discovered in samarskite. It is very similar to didymium.

Erbium (Er = 166) forms an oxide, Er_2O_3, of reddish color, and has not certainly been obtained as yet pure.

Terbium (Tb = 159.1) occurs in large amount in samarskite. The oxide has an orange-yellow color, and otherwise resembles the oxide of erbium.

These elements all form sesquioxides, but are not as closely related to aluminum, as they seem to form higher oxides also and several series of salts.

Three heavy metals also form a sub-group belonging in the same group of the periodic system as aluminum,—viz., gallium, indium, and thallium.

Gallium (Ga = 69.9) was discovered in zinc-blende in 1875 by means of the spectroscope. It also exactly corresponded with one of the hypothetical elements indicated as possible by Mendelejeff in his periodic system. It has been obtained by the electrolysis of an ammoniacal solution of its sulphate as a white, hard metal of sp. gr. 5.9 and fusing at 30°. It forms a true alum, $Ga_2(SO_4)_3 \cdot (NH_4)_2SO_4 + 24H_2O$.

Indium (In = 113.6) was discovered in 1863 by the aid of spectrum analysis in zinc-blendes from Freiberg. It is a silvery-white, soft, and tenacious metal of sp. gr. 7.42. It fuses at 176°, and when heated burns with a blue flame. The vapor-density of the chloride corresponds to the formula $InCl_3$. It forms, however, a true alum with ammonium sulphate.

Thallium (Tl = 203.7) is rather widely distributed in nature, being [illegible]g found in traces with potassium in carnallite, in mineral springs, and in [illegible] some pyrites and zinc-blendes. It was discovered in the chamber sludge [illegible] of the sulphuric-acid works by means of the spectroscope. It is a white [illegible] metal, as soft as sodium, and with a sp. gr. 11.8. It fuses at 290°, and [illegible] oxidizes rapidly in moist air. It burns with a beautiful green flame, [illegible] whose spectrum shows an intense green line, whence the name, from [illegible], green. It forms two series of salts, derived from Tl_2O and [illegible] Tl_2O_3.

The impure metal obtained is cast into ingots, which are subjected to a well-regulated heat, by which means the tin is mad to melt and run off, leaving behind, as a hard mass, any iron o copper present.

The final purification is effected by agitating the molten metal The lighter impurities rise to the surface and are skimmed of the heavier settle to the bottom of the vessel, and from these th tin is ladled off into ingot-moulds.

Properties.—Tin is dimorphous, crystallizing in forms belonging to the isometric and the quadratic systems. It has white, lustrous appearance, is a good conductor of heat an electricity, and, on account of the friction of its crystalline particles, it emits, when bent, a cracking sound, designated as th "cry of tin."

It is softer than zinc but harder than lead, with the exceptio of which its ductility is lowest of all the metals in common use, while in malleability it is surpassed by gold, silver, and coppe only.

At 100° its ductility is increased, and it may be drawn into wire; at 200° it becomes brittle, and may be powdered; and at 233° it melts, being the most fusible of common metals.

The specific gravity of the metal is 7.25. Metastannic acid is produced by the action of nitric acid upon tin. Hydrochloric acid dissolves it with evolution of hydrogen and formation of chloride, while strong alkalies act in a like manner with the production of metastannates.

Tin combines directly with most of the non-metals, the character of product depending on the conditions.

Uses.—In the form of granules or foil pure metallic tin is directed by the United States Pharmacopœia to be used for the preparation of fresh stannous chloride as a reagent. The best tin hammered to the proper thinness constitutes *tin-foil*, but ordinary tin-foil consists largely of lead.

Tinned-plate is sheet-iron superficially coated with the metal, those products having the very thick layers of the coating being known as *block-tin*. Copper protected by a film of tin furnishes a valuable material for the manufacture of culinary and other utensils. Pins are brass wire coated in the same manner.

Alloys of Tin.—Tin forms with lead the useful alloys *britannia metal*, *pewter*, and *solder*, and with copper *gun-metal*, *bronze*, *bell-metal*, *speculum-metal*, and *phosphor-bronze*, the latter owing its hardness and elasticity to several per cent. of tin introduced as phosphide.

stannic chloride is decomposed by an alkaline hydrate, or when a solution of a stannate is carefully precipitated by an acid. The stannic hydrate exhibits acid properties, reddening blue litmus paper. Heat decomposes it into water and stannic oxide.

Metastannic hydrate or acid, $H_{10}Sn_5O_{15}$, results when hot nitric acid acts on tin. It is distinguished from stannic acid by being altogether insoluble in nitric acid. Both compounds dissolve in alkalies to produce salts known as stannates and metastannates; the latter have complicated compositions.

OXYGEN SALTS OF TIN.

By far the most important compound of this class is sodium stannate, $Na_2SnO_3 + 4H_2O$. It is prepared either by fusing the stannic oxide with alkali, or the metal with alkali and sodium nitrate, or by dissolving the hydrated oxide in lye. Under the name of "preparing salts" it is extensively employed in calico-printing. The salt forms hexagonal crystals. The stannates of the alkali metals are soluble, those of the earthy and heavy metals insoluble, in water, and may be prepared by precipitation of the soluble stannates. The metastannates of the alkali metals are also used in dyeing. Stannous nitrate, stannous sulphate, stannic nitrate, and stannic sulphate are all recognized. The salts of tin possess an unpleasant metallic taste and an acid reaction.

TIN AND SULPHUR.

Stannous Sulphide, SnS, is obtained by heating together the metal and sulphur, or by precipitating a solution of stannous chloride with hydrogen sulphide.

When obtained by the first process it is a lead-gray, tough, crystalline mass; from the second method of preparation it is had as a brown precipitate, which becomes black on drying.

Stannic Sulphide, SnS_2.—This well-known compound is usually obtained by heating together tin-amalgam, sulphur, and sal-ammoniac, whereby it is obtained in gold-colored, translucent scales. It is used largely for bronzing articles of gypsum and wood, and is known as "mosaic gold."

TIN AND PHOSPHORUS.

Three phosphides of tin are known. They are respectively SnP, Sn_3P_2, and Sn_9P. The last is the only one made use of. It is a coarse, crystalline mass formed by the union of the proper quantities of the two elements, and is used for the production of phosphor-bronze.

GERMANIUM.

Symbol, Ge. *Atomic Weight*, 72.3. *Valence*, II and IV.

This extremely rare element was discovered in 1886 by Winkler in *argyrodite*, a silver ore mined at Freiberg.

Upon discovery it was found to possess the exact characteristics of the hypothetical eka-silicon, whose properties Mendelejeff, by the aid of his "Periodic Law," had predicted in 1871.

Germanic oxide, as also the hydrate, appears to possess acid properties.

On account of the unstable character of germanic sulphide it requires to be precipitated in the presence of considerable free hydrochloric acid.

When this compound is heated in a current of hydrogen, germanous sulphide, GeS, is produced. It may also be obtained as a red-brown precipitate by passing hydrogen sulphide into a solution of germanous chloride.

LEAD (Plumbum).

Symbol, Pb. *Atomic Weight,* 206.4. *Valence,* II and IV.

History.—Lead has been known from the earliest times. It was designated *Saturn* by the alchemists, who believed that some connection existed between the metals and the planets.

Occurrence.—Lead has been found in nature uncombined, but in small quantity only, as in certain volcanic tufa. The oxides of lead are found in a few rare minerals. By far the most abundant and important ore of lead is the sulphide or *galena*, PbS; this is very widely distributed, usually occurring with quartz, fluor-spar, calc-spar, and heavy spar. The most important deposits in England are those of Cornwall and Cumberland. In the United States there are two localities which furnish the chief supply of lead,—the Rocky Mountain district, in which the lead is a by-product in the preparation of silver, and the Mississippi Valley district, in which galena is worked for lead alone. The ores are known respectively as argentiferous and non-argentiferous, the former furnishing by far the greater proportion of lead. *Cerussite,* or native carbonate, $PbCO_3$, and *anglesite* or native sulphate, $PbSO_4$, are ores of minor importance when compared with galena.

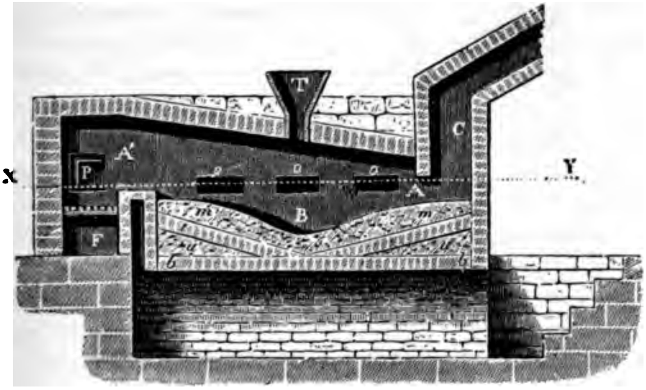
The total production of lead in the United States during 1893 amounted to 193,928 tons, valued at 14,467,029 dollars. The total production of the world during that time amounted to something over half a million tons.

Extraction.—Lead is almost exclusively prepared from galena. In case the ore is nearly free from other metallic sulphides and silica, it is roasted in a reverberatory furnace, whereby a part of the sulphide is converted into oxide and sulphate; air is then excluded, the temperature is increased, when the following reactions take place with formation of metallic lead:

$$PbS + 2PbO = 3Pb + SO_2.$$
$$PbS + PbSO_4 = 2Pb + 2SO_2.$$

This is known as the *air reduction process*, and is conducted in urnace as shown in Fig. 82. The furnaces are constructed to

FIG. 82.



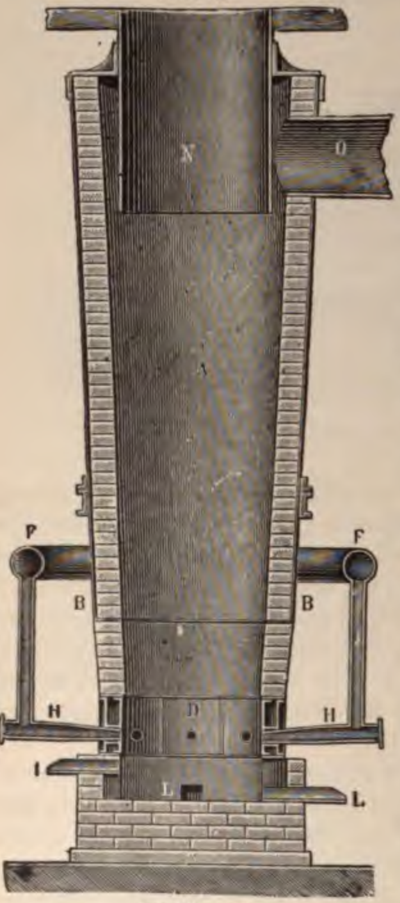
Lead furnace.

ld 20 tons of ore, which is introduced at T, and evenly spread er the hearth, which is hollowed out at B, so as to allow the tal to collect, and from which it can be drawn out by a tape into an iron pot. When the ore is impure, charcoal is used assist in the reduction. Small quantities of other metals are moved by melting the lead, and subjecting it to the oxidizing ion of a current of air in a reverberatory furnace. The imrities oxidize first, rise to the surface, and are removed as g.

ron is sometimes used as a reducing agent. This is accomshed by placing alternate layers of the ore and an iron slag a blast-furnace (Fig. 83). In this process a portion of the d is reduced by the metallic iron, a considerable residue, wever, remaining behind in the form of sulphide, together h the sulphides of iron and other metals contained in the . This slag or lead regulus is then worked up according to character of the metals of which it is composed. Sometimes pper is a constituent, in which case it may be so rich in that tal as to pay for extracting it.

When argentiferous lead ores are worked the process becomes dified according to the richness of the ore in silver, or the d is further treated. If silver predominates, the ore is oxidized d cupelled as described under that metal. It is much oftener the case that the lead predominates, when Pattinson's proc employed. This consists in cooling the melted metal, when lead first crystallizes ou is removed by perfo ladles. In this way a r very rich in silver is tained, which is cupell

FIG. 83.



Lead furnace.

Parke's process fo silvering lead is base the fact that melted and zinc do not mix i proportions. By ad therefore, a certain pr tion of zinc to the a tiferous lead, an allo zinc and silver is for which rises to the top solidifies. It is then e removed.

Properties.—Lead bluish-gray, lustrous m it is soft and malleable, is not capable of b drawn into wire. I easily cut with a knife, when drawn over w paper leaves a gray st Lead melts at 327.7°, quickly becomes co with a layer of oxide; red heat it vaporizes slo and when heated to w ness, distils. Melted crystallizes, when c slowly, in regular octohedrons. The specific gravity of le 11.37.

Pure water does not dissolve lead so long as air is exclu when, however, air is present, lead hydrate is formed, wh slightly soluble in water. Rain water and distilled water dissolve minute quantities of lead; hot water containing s proportions of various salts, notably chlorides and sulph does not dissolve the metal. With most natural waters, th fore, lead pipes may be employed. Carbonated waters should not be passed through such pipes, unless the latter are well tinned on the inner surface.

Concentrated hydrochloric or sulphuric acid attacks lead but slowly, even when warmed, but nitric acid dissolves it readily. Weak acids like acetic will dissolve it in the presence of air.

Uses.—On account of its power to resist the action of air, water, and acids, lead is employed for a great variety of purposes. Enormous quantities are used in the manufacture of lead pipe. It is also the best material for lining sulphuric acid chambers. Bullets and shot are made of lead; the latter contain one-half per cent. of arsenic in order to give them a spherical form.

Alloys of Lead.—Lead enters largely into the composition of a number of useful alloys. *Type-metal* is composed of 2 parts lead, 1 part each of antimony and tin. *Solder* consists of 1 part lead and 2 parts tin; a common variety is made of equal parts of these two metals.

LEAD AND OXYGEN.

Lead Suboxide, Pb_2O.—This compound is formed on the surface of melted lead when the temperature is not too high. It may be prepared by heating lead oxalate in an atmosphere free from oxygen and at a temperature below 300°. It is a black, velvety powder, which, if heated without access of air, decomposes into the metal and monoxide.

Lead Monoxide, PbO. **Plumbi Oxidum,** U. S. P. *Litharge.*—A rare mineral found near Vera Cruz is composed of this substance. There are two varieties of lead oxide in commerce,—namely, *massicot*, which is yellow in color and prepared by carefully heating lead carbonate or nitrate to low redness, and *litharge*, which has been prepared at a much higher temperature, and is a by-product in the desilverization of lead ores. Litharge is obtained at a temperature sufficiently high to fuse it, and in solidifying it forms shining, scaly masses, which are sometimes of a yellowish color, but oftener inclining to red.

Properties.—The official oxide is "a heavy, yellowish, or reddish-yellow powder, or minute scales, without odor or taste. On exposure to the air it slowly absorbs moisture and carbon dioxide." It is almost insoluble in water, but when left in contact with it imparts to it an alkaline reaction. It is insoluble in alcohol, but soluble in acetic and dilute nitric acids, and in solutions of sodium and potassium hydrates.

On the application of heat lead oxide assumes a brownish-red color, and at a red heat it fuses. When heated before the blowpipe on charcoal it yields metallic lead.

Uses.—Litharge is extensively used in the manufacture of flint glass, and is a constituent of the glaze used for earthenware. It is also useful as a starting-point for a number of other lead compounds.

Lead Sesquioxide,, Pb_2O_3, is formed as a reddish-yellow powder when cold solution of lead hydrate in sodium hydrate is mixed with a solution of sodium hypochlorite, or when a solution of red lead in acetic acid is precipitated by very dilute ammonia. It is decomposed by acids into the monoxide and dioxide, and is therefore considered to be a mixture of these two.

Red Lead or *Minium*, Pb_3O_4.—When litharge is carefully heated this oxide is formed. The commercial product is of variable composition. It is used as a pigment and in the preparation of the finer kinds of flint glass.

Lead Dioxide or *Peroxide*, PbO_2.—This is also known as *puce-colored lead oxide*. It is obtained by boiling lead acetate solution with solution of bleaching powder, or in the dry way by heating 4 parts of litharge with 8 parts of potassium nitrate and 1 part of potassium chlorate. It is also readily obtained by heating red lead with nitric acid.

Lead peroxide is a dark-brown, amorphous powder, which is readily decomposed by heat into lead monoxide and oxygen. It occurs native in black, hexagonal prisms as *plattnerite*. Lead peroxide has a strong oxidizing action on many compounds, especially those of an organic character.

Lead Hydrate, $Pb(OH)_2,PbO$.—This is more properly called oxyhydrate. It is obtained as a white precipitate when solution of lead acetate or nitrate is treated with so much solution of sodium or potassium hydrate as is necessary to produce an alkaline reaction. It is insoluble in water, but easily soluble in excess of sodium or potassium hydrate, forming the compounds $Pb(ONa)_2$ and $Pb(OK)_2$. When solutions of these are boiled the yellow or red lead oxide separates according to the concentration of the solution.

LEAD AND THE HALOGENS.

Lead Chloride, $PbCl_2$, is found to some extent in nature as the mineral *cotunite*. It is most readily prepared by adding sodium chloride to a solution of lead nitrate or acetate, although it may be obtained by dissolving lead in hot aqua regia.

Lead chloride occurs in white, pearly crystals, soluble in 135 parts of cold water and in about 30 parts of that liquid at the boiling temperature. At 498° the crystals melt, and on cooling form a horny mass.

A number of oxychlorides are known which are employed as pigments; *Cassel's yellow* is one of these; it is prepared by heating together lead oxide and sal-ammoniac. The oxychloride, $PbO,PbCl_2$, is found in nature as the mineral *matlockite*.

other lead compounds in the manufacture of paint and in the manufacture of lead chromate.

Lead Nitrate, $Pb(NO_3)_2$. **Plumbi Nitras, U. S. P.**

Preparation.—This salt is prepared by adding, in small portions at a time, 10 parts of lead oxide to 23 parts of nitric acid (25 per cent.), previously mixed with an equal weight of water and warmed:

$$PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O.$$

The solution is filtered, and, after the addition of a few drops of nitric acid, is set aside to crystallize.

Properties.—Lead nitrate crystallizes in large, anhydrous regular, mostly octohedral crystals, isomorphous with the nitrate of barium and strontium. When these crystals separate from hot solutions they are white and opaque, but if formed by the spontaneous evaporation of cold solutions they are transparent. The salt is soluble in 2 parts of water and in 0.75 part of boiling water; almost insoluble in alcohol. On the application of heat nitrous fumes are evolved and a residue of lead oxide remains.

Uses.—Lead nitrate is used extensively in the manufacture of mordants for use in dyeing and calico-printing, and in the manufacture of lead chromate.

Lead Nitrite, $Pb(NO_2)_2$, is obtained by decomposing silver nitrite with lead chloride. The solution is concentrated in a vacuum, when yellow, prismatic crystals separate, which are readily soluble in water.

Lead Phosphate, $Pb_3(PO_4)_2$, forms as a white precipitate when solutions of lead acetate and sodium phosphate are mixed. When phosphoric acid is added to a boiling lead nitrate solution, lustrous, white crystals having the composition $PbHPO_4$ separate.

Lead Borates.—A number of these salts appear to exist, one of which is obtained by precipitating a soluble lead salt with solution of borax. It appears to have the composition $Pb_2B_6O_{11}.4H_2O$.

Lead Silicates.—These compounds are formed in the manufacture some kinds of glass. When equal weights of lead oxide and silica are fused together a yellow glass is formed.

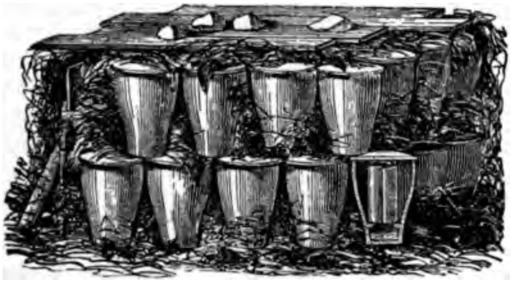
Lead Carbonate, $PbCO_3$.—The normal lead carbonate is found nature as the mineral *cerussite*, or it may be artificially prepared by precipitating a solution of lead acetate with one of ammonium carbonate. This compound is not much used.

Basic Lead Carbonate, $(PbCO_3)_2Pb(OH)_2$. **Plumbi Carbonas, U. S. P.** *White Lead.*—This compound was known the ancients.

Preparation.—White lead is manufactured on a large scale by the following processes:

1. *The Dutch Process* is the oldest, and is employed in Holland, Belgium, and some parts of Germany. It consists in placing coils or buckles of lead in earthenware pots, in the bottom of which is a small quantity of vinegar. The lead is placed on projections in the pots so as not to come in direct contact with the liquid; the walls of the pots are perforated just above the vinegar, so as to allow a free circulation of air and gas. A number of the pots are placed together as shown in Fig. 84, and after covering each with a wooden plate they are surrounded with horse manure or spent tan-bark. The fermentation of the manure or tan causes the requisite elevation of temperature to vaporize some of the acetic acid of the vinegar, which acts on the lead with the formation of basic lead acetate. This is slowly converted into carbonate by the carbon dioxide which results from the fermentation. After some weeks the lead will be found wholly converted into basic carbonate.

FIG. 84.



Dutch process for making white lead.

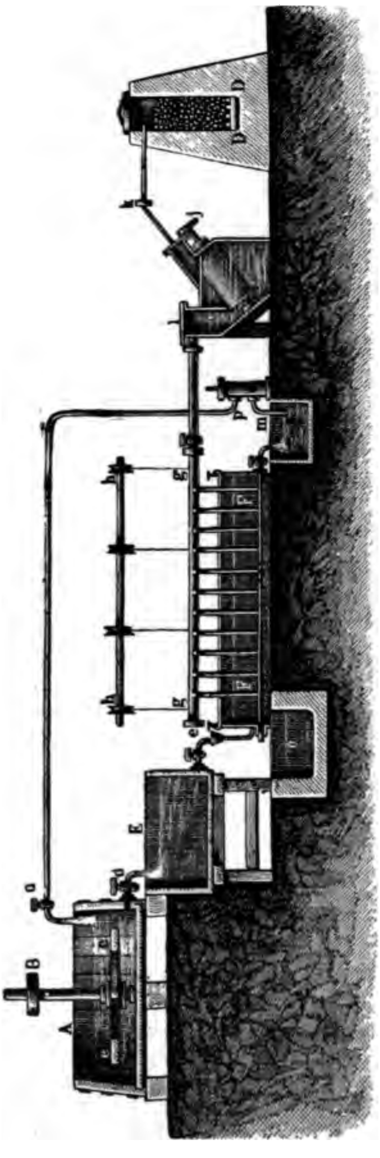
2. In the *English Method* sheet-lead is melted on the hearth of a reverberatory furnace so as to convert it into oxide, and this in turn is intimately mixed with a small quantity of solution of lead acetate. The resulting mass is placed in a series of closed troughs communicating with one another, and so arranged as to admit the passage of a current of carbon dioxide. This gas is obtained by the combustion of coke in a furnace provided with a blast to give impulse to the gas.

3. The *German* or *Austrian Method* involves the action of acetic acid and carbon dioxide on sheets of lead as in the Dutch process, but a large number of the lead coils are placed in a room with vinegar and tan on the floor. The tan is caused to ferment and furnish the necessary carbon dioxide.

4. The *French Method* consists in dissolving an excess of lead or lead oxide in acetic acid, so as to form basic lead acetate, and then passing carbon dioxide into this solution, by which means two molecules of lead oxide are converted into basic carbonate, while neutral acetate of lead remains. This is again converted into basic acetate, which is, in turn, decomposed by more carbon dioxide.

The principle involved in this method was first explained by Thénard, but it is generally known as the *Clichy Process*, because of the works located at Clichy, near Paris. Fig. 85 shows a plan of these works. In the tub A, the litharge is dissolved in acetic acid, the solution being aided by means of the stirrer *e e*. The solution of basic lead acetate is run into the vessel E, where the impurities subside, and the clear solution is then run into the decomposing vessel F F, which is supplied with several hundred tubes for the admission of the carbon dioxide. In 12 to 16 hours the conversion is complete. The neutral lead acetate is run into the tank *m* and returned to A, while the semi-liquid basic lead carbonate is drawn into the tank O. The carbon dioxide is generated in D and purified in the vessel *j*.

FIG. 85.



The Clichy white-lead process.

Many more processes have been patented and worked in a small way in the production of white lead, but it is probable that in this country, as well as in most foreign countries, the Dutch method is given the preference.

The product in all the foregoing processes is finely ground with water, well washed to remove lead acetate, and finally dried.

Some white lead is made from lead sulphate by heating together this salt and solution of sodium hydrate, whereby a basic lead sulphate is formed, and this, by boiling with sodium carbonate solution, is converted into basic lead carbonate and sodium sulphate.

Properties.—Basic lead carbonate is a heavy, white, amorphous powder. It is without odor or taste, and is permanent in the air. Water and the other ordinary solvents do not

ZIRCONIUM.

Symbol, Zr. *Atomic Weight*, 90.4. *Valence*, IV.

Zirconium is relatively rare, being generally found as the silicate, $ZrSiO_4$, called *Zircon*. The metal can be obtained as an amorphous black powder or in crystalline metallic leaflets.

Zirconic Acid or *Hydrate*, $Zr(OH)_4$, is precipitated from acid solutions as a white, voluminous precipitate, which, on ignition, leaves

Zirconium Dioxide, ZrO_2.—Both this oxide and the hydrate dissolve when warmed with sulphuric acid, forming $Zr(SO_4)_2$, which may be crystallized from water.

THORIUM.

Symbol, Th. *Atomic Weight*, 231.9. *Valence*, IV.

Thorium occurs only in rare silicates, such as *thorite*. The free metal has been obtained as a light-gray, crystalline powder which burns in the air to the dioxide.

Thorium Hydrate, $Th(OH)_4$, and *Thorium Dioxide*, ThO_2, do not form salts with the alkalies, but dissolve in sulphuric acid to form $Th(SO_4)_2$.

CHAPTER VIII.

THE ARSENIC GROUP.

ARSENIC.

Symbol, As. *Atomic Weight,* 74.9. *Valence,* III and V.

History.—Arsenic in the form of its two sulphides, *realgar* and *orpiment,* was known to the ancients. Schroeder, in 1694, appears to have been the first to separate the metal.

Occurrence.—Arsenic is widely distributed in nature; in the free state it is occasionally found in distinct crystals, but oftener in kidney-shaped masses, which readily split into laminæ. Native arsenic has been found in Saxony, Bohemia, and various other parts of Europe, at San Augustin, in Mexico, and at Haverhill, New Hampshire, in the United States. In the combined state arsenic is more abundantly distributed; as white arsenic, As_2O_3, as orpiment, As_2S_3, and as realgar, As_2S_2, it is well known; but its most important occurrence is in the form of arsenical iron, $FeAs_2$, and arsenical pyrites or mispickel, $FeAs_2,FeS_2$. Certain cobalt and nickel ores also contain considerable quantities of arsenic. Small quantities of arsenic are found in many mineral waters and in sea water.

Preparation.—Metallic arsenic is prepared by subliming the native mineral or by reducing arsenous oxide with charcoal:

$$As_2O_3 + 3C = 2As + 3CO.$$

Probably the largest quantity is prepared by subliming arsenical pyrites:

$$FeAs_2,FeS_2 = 2As + 2FeS.$$

Properties.—Arsenic is a steel-gray, lustrous metal, which occurs in several allotropic modifications. When heated quickly in a tube through which hydrogen is passing, there separate nearest the heated portion of the tube distinct crystals; next to these the metal deposits in a black, amorphous mass, and still farther away a gray, amorphous powder is condensed. The crystalline variety has a specific gravity of 5.727, while that of the two amorphous varieties is 4.710. The amorphous varieties become crystalline when heated to 360°. In dry air arsenic undergoes no change, but in moist air it becomes oxidized in part to arsenous oxide. When heated in air the metal burns to arsenous oxide, but when heated without access of air, it vaporizes without previously melting.

Uses.—Metallic arsenic is chiefly used in the manufacture of shot to give a globular form to the grains. Cobalt glance, a compound of arsenic and cobalt, has considerable use as a fly-poison under the name of *fly-stone.*

ARSENIC AND HYDROGEN.

Hydrogen Arsenide or *Arsine*, AsH_3.—In order to prepare arsine in a pure state, an alloy of zinc and arsenic, As_2Zn_3, is treated with dilute sulphuric acid:

$$As_2Zn_3 + 3H_2SO_4 = 2AsH_3 + 3ZnSO_4.$$

This reaction should be carried out with the greatest care, as the gas is extremely poisonous. Gehlen lost his life by it in 1815. Arsine is a colorless, disagreeably-smelling gas, which when once ignited burns in the air with the formation of arsenous oxide and water. If the flame be cooled by the introduction of a cold, porcelain surface, black, shining, metallic arsenic is deposited. *Marsh's test* (see Qualitative Test, Part V.) depends on this property. When arsine is passed into a solution of silver nitrate, metallic silver is precipitated as follows:

$$6AgNO_3 + AsH_3 + 3H_2O = 3Ag_2 + 6HNO_3 + H_3AsO_3.$$

If the gas be passed through a tube and flame be applied at one point so as to bring the tube to low redness, the gas is decomposed and a brilliant layer of metallic arsenic is deposited; this also serves as a method of detecting the element.

Solid Hydrogen Arsenide, As_2H_2, is formed as a brown, silky mass when sodium arsenide, $AsNa_3$, is decomposed by water.

ARSENIC AND THE HALOGENS.

Arsenic Trichloride, $AsCl_3$, may be prepared by passing dry chlorine over powdered arsenic; but it is more easily obtained by heating to the boiling point of water 40 parts of arsenous oxide with 100 parts of concentrated sulphuric acid in an apparatus connected with a well-cooled receiver; small pieces of fused sodium chloride are then thrown in, when the following reaction takes place:

$$6HCl + As_2O_3 = 2AsCl_3 + 3H_2O.$$

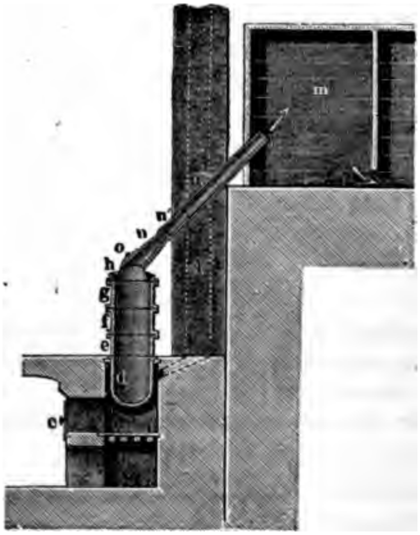
The water which is liberated is retained by the sulphuric acid.

Properties.—Arsenic trichloride is a colorless, oily liquid, having a specific gravity of 2.205. It boils at 134°, forming a colorless vapor. When brought in contact with a large quantity of water, the oxychloride, $As(OH)_2Cl$, separates.

Arsenic Tribromide, $AsBr_3$, forms colorless, deliquescent crystals, which melt at 20° to 25°, and the resulting liquid boils when heated to 220°.

vessel in which the oxide is heated; on this are placed a number of iron cylinders, *e*, *f*, *g*, *h*, which are connected by the tubes *o*, *n*, *n'*, with the chamber *m*. In the cylinders the oxide condenses as an amorphous, opaque, glassy solid, while in the tubes and chambers it is deposited as a crystalline powder.

FIG. 86.



Sublimation of arsenous oxide.

Properties.—Arsenous oxide occurs in two modifications, amorphous and crystalline; the former is transparent and colorless like glass, while the latter is opaque or white, resembling porcelain. The glassy variety gradually changes to the opaque form. Both are odorless and tasteless.

"In cold water both varieties dissolve very slowly, the glassy variety requiring about 30, the porcelain-like about 80 parts of water at 15°. Both are slowly and completely soluble in 15 parts of boiling water. In alcohol, Arsenous Acid is but sparingly soluble, but it is soluble in about 5 parts of glycerin. Oil of turpentine dissolves only the glassy variety. Both varieties are freely soluble in hydrochloric acid, and in solutions of alkali hydrates and carbonates."

On the application of heat the oxide volatilizes completely at 218° without melting, and if its vapor be passed over charcoal in a tube, it is reduced to the metal and deposited on the glass as a mirror.

Arsenous Acid, H_3AsO_3, is not known in the free state, but when arsenous oxide is dissolved in water it imparts to the latter a feebly acid reaction. The following salts are the most important:

Potassium Arsenite. **Liquor Potassii Arsenitis, U. S. P.**—The official process consists in boiling 10 grammes of arsenous oxide with 20 grammes of potassium bicarbonate and 100 c.c. of water until a clear solution is effected, and then dilut sufficient water and 30 c.c. of compound tincture of lavender to make 1000 c.c. The product is used in medicine under the name of *Fowler's solution.* Only the alkali arsenites are soluble in water.

Cupric Arsenite, $CuHAsO_3$, *Scheele's Green*, is an insoluble green powder used as a pigment.

Paris Green is a cupric aceto-arsenite made by boiling together solutions of copper acetate and arsenous oxide. It has the formula $Cu(C_2H_3O_2)_2.3Cu(AsO_2)_2$.

Arsenous oxide is one of the compounds most frequently employed as a poison. Its action may be deferred or neutralized by large doses of freshly precipitated ferric hydrate.

ARSENIC OXIDE AND ARSENATES.

Arsenic Oxide, As_2O_5, *Arsenic Pentoxide*, is prepared by heating arsenic acid to low redness. It forms a white, fusible, glassy mass. By a strong heat it is converted into arsenous oxide and oxygen.

Arsenic Acid, H_3AsO_4, *Orthoarsenic Acid*, is obtained by long boiling of arsenous oxide and nitric acid. The solution is evaporated to a syrupy consistence, when crystals separate having the composition $(H_3AsO_4)_2.H_2O$. These crystals deliquesce in the air, and give up their water of crystallization at 100°. On heating to 180° they lose additional water and are converted into pyroarsenic acid, $H_4As_2O_7$, and at 200° a pearly, lustrous mass of meta-arsenic acid, $HAsO_3$, is formed.

Arsenic acid has some use as an oxidizer in the preparation of a number of the aniline colors.

Sodium Arsenate, $Na_2HAsO_4.7H_2O$. **Sodii Arsenas,** U. S. P. —This official salt may be prepared by neutralizing arsenic acid with sodium carbonate, but the process given by the Pharmacopœia of 1870 is more economical; this consists in fusing together in a clay crucible 10 parts of arsenous oxide, 8.5 parts of sodium nitrate, and 5.5 parts of dried sodium carbonate. The fused product is poured while hot on a porcelain slab, dissolved in water, the solution filtered, and set aside to crystallize. The reaction involved is as follows:

$$As_2O_3 + 2NaNO_3 + Na_2CO_3 + H_2O = 2Na_2HAsO_4 + N_2O_3 + CO_2.$$

The crystals should be kept in well-stoppered bottles; they effloresce in dry air, and are somewhat deliquescent in moist air.

Properties.—Sodium arsenate occurs in colorless, transparent, monoclinic prisms. It is soluble in 4 parts of water at 15° and very soluble in boiling water; very sparingly soluble in cold alcohol, but dissolved by 60 parts of that liquid when boiling. On the application of a gentle heat the salt loses 5 molecules of water, amounting to 28.8 per cent., at 148° the remainder of the water is given off, the salt melts, and at a red heat is converted into pyroarsenate.

Monobasic Sodium Arsenate, $NaH_2AsO_4.H_2O$, and *Tribasic Sodium Arsenate*, $Na_3AsO_4.12H_2O$, are known.

ARSENIC AND SULPHUR.

Arsenic Disulphide, As_2S_2, *Realgar*, is found native, crystallized in oblique rhombic prisms.

It is prepared by melting together 15 parts of metallic arsenic and 6.5 parts of sulphur, or by the sublimation of 4 parts arsenous oxide and 2 parts sulphur. The product occurs in red, glassy masses, translucent on the edges. It is insoluble in water, but is readily dissolved by the alkali sulphides.

Realgar is used as a coloring, in the manufacture of leather, and in the preparation of *white* or *Indian fire*. This consists of 24 parts saltpetre, 2 parts realgar, and 7 parts sulphur.

Arsenic Trisulphide, As_2S_3, *Orpiment*.—Under the latter name this compound is found in nature, crystallized in lemon-colored, rhombic prisms. It is prepared by melting together 6 parts of metallic arsenic and 4 parts of sulphur, or by subliming a mixture of 4 parts of arsenous oxide and 3 parts of sulphur. This compound is also formed when hydrogen sulphide is passed into a hydrochloric acid solution of arsenous oxide. It is melted to a yellowish-red liquid when heated, and at 700° volatilizes without decomposition.

When dissolved in the alkali sulphides it forms arsenites and thioarsenites as follows:

$$2As_2S_3 + 4KOH = KAsO_2 + 3KAsS_2 + 2H_2O.$$

On the addition of hydrochloric acid, the whole of the arsenic is reprecipitated as sulphide:

$$KAsO_2 + 3KAsS_2 + 4HCl = 2As_2S_3 + 4KCl + 2H_2O.$$

The *sulpharsenites* or *thioarsenites* constitute a class of compounds which bear the same relation to arsenic trisulphide as the arsenites bear to arsenous oxide.

Arsenic Pentasulphide, As_2S_5, is obtained by fusing arsenic trisulphide with the proper proportion of sulphur, or by precipitating a dilute solution of sodium or ammonium sulpharsenate with hydrochloric acid. It is a yellow, fusible mass which may be sublimed without decomposition, provided air is excluded.

The *thioarsenates* or *sulpharsenates* form a class of compounds, the members of which are prepared by dissolving arsenic pentasulphide in an alkali sulphide, or by precipitating an arsenate with hydrogen sulphide.

THE DETECTION OF ARSENIC IN ANIMAL TISSUES.

On account of the ease with which it may be obtained and the certainty of its action, arsenic figures in more cases of poisoning, both accidental and intentional, than any other substance.

Where some of the powdered material is obtained from the stomach in a comparatively pure form, the identification of it is quite easy. It is simply necessary to employ the usual qualitative reactions. But oftener the poison has been absorbed by the system, and it is necessary to separate it from the tissues, or it is so intimately mixed with the contents of the stomach as to make any preliminary separation impossible. The stomach and its contents, and sometimes the other organs, are cut finely and triturated in a porcelain mortar until a uniform mass is obtained. This is then placed in a clean porcelain evaporating dish, and an equal volume of hydrochloric acid, having a specific gravity of 1.12, is added. The whole is heated on a water-bath, and every five minutes from one to two grammes of potassium chlorate are added. This is continued until a thin, yellowish liquid is obtained; after the addition of a few more grammes of the chlorate, the heat is continued until all odor of chlorine has disappeared. The liquid is filtered, warmed to 70°, and treated for a considerable time with hydrogen sulphide. This sulphide may be collected, washed, dissolved, and detected by the usual arsenic reagents and tests as described in Part V. of this work. The method as given serves for the separation of a number of other metals that are sometimes used as poisons, and they may then be detected by the appropriate tests.

It is of the greatest importance to employ in this operation dishes and reagents that are absolutely free from the presence of traces of contamination. Therefore a blank experiment should first be carried out to prove the absence of impurities.

ANTIMONY (Stibium).

Symbol, Sb. *Atomic Weight*, 119.6. *Valence*, III and V.

History.—Although long before his time the ores of antimony, and probably the metal itself, were known to the alchemists of the East, the initiative step to the present knowledge of the element was reserved for Basil Valentine, who about the middle of the fifteenth century prepared and described not only the metal, but also a number of its compounds. At the same time he pointed out the value of the metal for the preparation of medicines and of alloys. A century later, however, Libavius confounded antimony with bismuth.

In the early part of the present century, Thénard, Proust, and particularly Berzelius, added to the positive literature of this metal. The names given to the element at present are the Chaldean term, *stibium*, and the Latin title, *antimonium*, both of which were applied to the native sulphide until the time of Lavoisier.

Occurrence.—The chief source of antimony is the mineral *stibnite*, Sb_2S_3, which has been known since early history, but the metal also occurs directly combined with arsenic, nickel, and silver; and, though infrequently and in small quantities only, antimony is found in the free state associated with the preceding forms. As oxide, Sb_2O_3, we have the element occurring as octohedral crystals, *senarmontite*, and in rhombic prisms, *valentinite*. Of other antimony ores may be mentioned those in which the trisulphide, Sb_2S_3, forms thio-antimonates, or the so-called *sulpho-salts*, with the sulphides of such metals as copper, iron, lead, and silver, in which arsenic often replaces part of the antimony.

Stibnite is found extensively in Canada and in Hungary; considerable antimony ore enters commerce from Cornwall, Algiers, Borneo, Nevada, South America, and New Brunswick.

Preparation.—To separate antimony from the accompanying minerals advantage is taken of the easy fusibility of the sulphide, which is heated in vertical cylinders having holes at the bottom for the egress of the molten sulphide; or this preliminary fusion is carried on in reverberatory furnaces. To obtain the metal, the purified sulphide formed as above described is either fused with metallic iron,

$$Sb_2S_3 + 3Fe = 2Sb + 3FeS,$$

or is roasted to form oxide, which is afterwards reduced with charcoal and sodium carbonate, or with crude tartar, as follows:

$$2Sb_2S_3 + 3C + 6Na_2CO_3 = 2Sb_2 + 9CO_2 + 6Na_2S.$$

The availability of the reactions of both methods was known to Basil Valentine.

The process employed in England, where much of the antimony of commerce is prepared, comprises three successive stages, —viz., "singling," which consists in melting the sulphide with one-half its weight of scrap-iron for an hour and a half in plumbago crucibles; "doubling," whereby the metallic antimony, which was separated from the slag of iron sulphide formed in the first operation, is fused for the same time with 2.5 per cent. each of sodium sulphate and a slag consisting principally of pearl-ash; and "melting for stove-metal" with a previously used slag of the last substance and an additional quantity of fresh pearl-ash for a similar period.

The metal is then poured into square moulds, its surface covered with slag, and the molten mass allowed to cool slowly to insure the peculiar crystalline structure which is required in commerce. The antimony so obtained may contain arsenic, from which it is freed by fusion with sodium carbonate and potassium nitrate, sometimes with the addition of a small quantity of antimony trisulphide, and subsequent reduction of the lixiviated mass by charcoal and sodium carbonate.

Properties.—Antimony is a lustrous, silver-white metal, more basic than arsenic but less so than bismuth. It is harder than the last metal, and like it crystallizes in obtuse rhombohedra, a mass of which exhibits a granular or a coarsely laminated, fern-marked, crystalline fracture, according as it is rapidly or slowly cooled. This structure determines the great brittleness of the metal. Antimony has a specific gravity of 6.7, is scarcely tarnished by air, melts at 432°, volatilizes at a bright red-heat, and can be distilled in hydrogen at a white-heat. On charcoal, before the blow-pipe it melts and evolves white fumes of trioxide, and, if the globule of molten metal is dropped from some height, it scatters in many small particles, which burn with a very bright flame to trioxide. At ordinary temperatures, cold water does not act upon the element, which, however, at a red-heat decomposes steam. Hot, but not cold, hydrochloric and sulphuric acids, as also cold nitro-hydrochloric acid, dissolve antimony.

Nitric acid converts the metal into white antimony trioxide, Sb_2O_3, and antimonic acid, H_3SbO_4; while solutions of the alkali hydrates produce no change. It combines directly with the halogens, and with sulphur, phosphorus, and arsenic. The existence of an amorphous allotropic modification of this element in the so-called explosive antimony obtained by the electrolysis of strong solutions of the compounds of the metal is still a matter of doubt.

Uses.—From the metal a chloride, suitable for the preparation of some of the medicinal compounds, is prepared, but the largest amount of antimony is used in the trades and manufactures in the form of alloys or of compounds. Along with bismuth, antimony finds use in the construction of thermo-electric piles.

When antimony is precipitated from a solution of the trichlo by zinc, the metal is obtained in a finely pulverulent condit In this state it is called *antimony-black*, and is used to im to the surface of gypsum and papier-maché figures and o objects the appearance of iron or steel.

Alloys.—These are useful because of their hardness and easy fusib *Type-metal* contains besides lead, and sometimes small quantities of about 20 per cent. of antimony. Such an alloy expands upon coo from the state of liquefaction, although its separate component elem when congealing shrink.

Britannia-metal consists of approximately nine parts of tin and part of antimony, often with some addition of copper, zinc, and bism

By the use of antimony superior *pewter* and *anti-friction-metal* are the latter is used extensively for machinery bearings, and like the for is an alloy of the metal with tin, or with tin and lead.

ANTIMONY AND HYDROGEN.

Hydrogen Antimonide (*Stibine*), SbH_3, is formed when nascent hy gen is brought in the presence of acid into contact with finely div antimony or any compound of it that is capable of reduction by the Obtained in the usual way by the action of dilute sulphuric acid on zi the presence of an antimony compound, it is mixed with much hydro and apparently remains unaltered for a long time; but when gener in more concentrated form by slowly adding a nearly saturated solu of antimony in strong hydrochloric acid to an excess of granulated the compound soon decomposes.

The pure gas has probably never been prepared. That yielded by processes given is colorless, has a disagreeable smell and taste, and b with a bluish-white or grayish flame, evolving white fumes of antin trioxide.

If a cold porcelain plate is pressed into the flame, a sooty depos metallic antimony is obtained.

Hydrogen antimonide is decomposed if passed through a red-hot t metallic antimony being deposited close to the heated spot. If deposit be heated the minute particles coalesce to form microsc globules.

These metallic spots are distinguished from those produced unde same conditions by arsenic by the darker color of the former, smoky appearance, their lesser volatility, their insolubility in hypochl solutions, and their solubility in ammonium sulphide.

Strong sulphuric acid decomposes the gas, as does also alkali hyd solutions; the latter behavior accounts for the failure of antimon produce its hydrogen compound in Fleitman's test, wherein the ne sary nascent hydrogen is evolved from zinc and potassium hydrate, whereby arsenic may be detected.

When hydrogen antimonide is conducted into a solution of si nitrate, a black precipitate containing silver antimonide, $SbAg_3$, and some metallic silver arising from the reduction of the silver salt by the hydrogen present, is thrown down.

ANTIMONY AND THE HALOGENS.

Antimony Trichloride, $SbCl_3$.—This was long ago prepared by subliming antimony sulphide with corrosive sublimate. It may be obtained by distilling the sulphide with hydrochloric acid, or with materials yielding it, as follows:

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

The metal or sulphide by the action of dry chlorine and heat will also furnish it.

The trichloride forms a deliquescent crystalline mass known as *butter of antimony*, which melts at 72°, and boils at 223°. The solution of the chloride (*liquid butter of antimony*) is best made by boiling the trisulphide with strong hydrochloric acid, and evaporating to remove water and excess of acid. This solution is occasionally used in medicine as a caustic; but it is extensively employed for giving a bronze surface to iron and steel wares, such, for instance, as gun-barrels. The color of the solution made from sulphide is due to ferric chloride produced from the iron present.

When the solution of the chloride is mixed with water there is thrown down an amorphous, white precipitate of the basic chloride, which, by standing in contact with the accompanying liquid, becomes crystalline.

The composition of the product varies according as it is produced by cold or hot water; the former yields SbOCl, the latter $Sb_4O_5Cl_2$; whereas the presence of free hydrochloric or of tartaric acid prevents the precipitation. These compounds were much used towards the end of the sixteenth century by a Veronese physician, Algarotus, hence the name *powder of Algaroth*, by which the dry substances are often designated.

Antimony Pentachloride, $SbCl_5$, results from the direct union of antimony and chlorine, and upon saturation of the fused trichloride with chlorine gas. It is a colorless, hygroscopic, fuming, disagreeably-smelling liquid, which solidifies at a temperature below 0°, and is decomposed by water.

This compound is used as a chlorinating agent in the preparation of certain organic chlorides.

Antimony Tribromide, $SbBr_3$.—Like chlorine, bromine combines with antimony with the evolution of light and heat. The resulting compound sublimes in colorless, deliquescent needles, which melt at 90°, boil at 275°, and are changed by water to basic bromide.

The tribromide is obtained in octohedra by heating an excess of powdered antumony with a solution of bromine in carbon disulphide and evaporating the solution.

A pentabromide is not known.

Antimony Tri-iodide, SbI_3, is a brownish-red crystalline mass obtained by directly uniting iodine and antimony with the aid of heat. It is sublimable, and altered by water, with the formation of yellow basic iodide.

The existence of a penta-iodide has not been satisfactorily established.

Antimony Trifluoride, SbF_3, is a snow-white mass procured by distilling antimony with mercuric fluoride, or by evaporating a solution of the oxide in excess of hydrofluoric acid.

The product is deliquescent, but not decomposed by water, although if a solution which is destitute of free acid is evaporated a basic compound is produced.

A pentafluoride, SbF_5, can be had by dissolving antimonic acid in hydrofluoric acid.

All the above halogen combinations yield with the corresponding compounds of the alkali metals crystallizable double salts.

ANTIMONY AND OXYGEN.

Antimony Trioxide, Sb_2O_3. **Antimonii Oxidum, U. S. P.**—As mentioned under the occurrence of antimony, this oxide is found native in the crystalline form, often colored by the presence of iron and other metals. It is isodimorphous with arsenic trioxide. A mixture of the two forms is obtained upon heating the metal to a red heat, while the octohedral variety can be produced by subliming the rhombic into which it again reverts when strongly heated.

On a small scale the oxide is usually prepared by pouring a solution of the trichloride into a boiling solution of sodium carbonate or into water. In the latter instance the precipitate of basic chloride is treated with solution of sodium hydrate to decompose it, and the resulting oxide finally washed with water, which alone is required when the use of sodium carbonate is involved in the process, the trichloride yielding oxide by reaction with that salt in the presence of hot water. In both cases the washed product is carefully dried. Antimony trioxide so prepared is "a heavy, grayish-white powder without odor or taste, and permanent in the air.

"Almost insoluble in water, and insoluble in alcohol. Nitric acid fails to dissolve it, but it is readily soluble in hydrochloric acid without effervescence, and also in a warm solution of tartaric acid, or in a boiling solution of potassium bitartrate. When heated the oxide turns yellow, becoming white again on cooling, and at a dull red heat fuses to a yellowish liquid, which concretes, on cooling, to a crystalline mass of a pearly color.

"At a higher temperature it sublimes, producing colorless and transparent, or white, shining, needle-shaped crystals."

This compound is used in the preparation of tartar emetic, which is a double tartrate of antimonyl and potassium. To a more limited extent it is itself employed in the practice of medicine, but the largest consumption of it is in painting, where it is used as a substitute for white lead. For the last purpose the oxide is prepared by roasting the metal or sulphide in air.

Antimonous Acid, H_3SbO_3, separates as a white precipitate when weak sulphuric or nitric acid is cautiously added to tartar emetic solution. When dry it is a fine, white powder.

Metantimonous Acid, $HSbO_2$, is obtained as a white, amorphous precipitate when antimony trichloride is decomposed with a solution of potassium hydrate or carbonate, in the former of which, when applied in excess, it redissolves. Hot water decomposes it into trioxide. With alkalis it acts the part of an acid, although it saturates acids to give salts of antimony containing the group, SbO, usually termed *antimonyl.*

Antimony Tetroxide, Sb_2O_4.—This has been regarded as composed of both antimony trioxide and antimony pentoxide, for the reason that when treated with tartaric acid solution the former is dissolved while the latter remains. The structural formulas proposed are $Sb_2(SbO_4)_2$ and $(SbO)SbO_3$; the first would be called antimony antimonate, the second antimonyl metantimonate. This substance results when either of the other oxides is ignited. When heated it becomes yellow, but when cold it is white. When heated with potassium hydrate a compound known as potassium hypoantimonate, and having the formula $K_2Sb_2O_5$, is left upon washing out the fused mass with cold water.

Antimony Pentoxide, Sb_2O_5, is obtained by heating antimonic acid or by evaporating the metal, or trioxide, with nitric acid and gently heating the residue. It is a yellowish, tasteless powder, which is soluble in hydrochloric acid, but not in water. Like arsenic oxide, it forms hydrates which have acid characters. They are antimonic acid, H_3SbO_4, pyroantimonic acid, $H_4Sb_2O_7$, and metantimonic acid, $HSbO_3$. The second of those named is usually termed metantimonic acid, and the last antimonic acid, but that their relationship to the acids of arsenic may be more readily seen, the names applied to the latter are used here.

Antimonic Acid, H_3SbO_4, is produced when antimony pentachloride is added by drops to cold water. Thus obtained it is a gelatinous precipitate possessing a metallic, astringent taste and a distinct acid reaction.

At 100° it loses water, and is changed to pyroantimonic acid, $H_4Sb_2O_7$, which is more soluble in water than antimonic acid. It also dissolves in ammonium hydrate, forming ammonium pyroantimonate, $(NH_4)_4Sb_2O_7$, which exists only in solution.

Potassium Pyroantimonate, $K_4Sb_2O_7$, is obtained by fusing the gelatinous metantimonate with three times its weight of potassium hydrate, dissolving the fused mass in water, and evaporating. It is not stable.

The *Acid Sodium Salt*, $Na_2H_2Sb_2O_7 + 6H_2O$, is remarkable as being the only insoluble compound of sodium, and its formation is sometimes used as a test for that element, but necessarily only in the absence of other metals.

Metantimonic Acid, $HSbO_3$, remains when pyroantimonic acid loses water at 200°, or when powdered antimony is evaporated with nitric acid and the residue washed. It is also formed by evaporating the potassium salt with excess of nitric acid and washing the product so obtained. It is a white, infusible powder, which is insoluble in water, but soluble in tartaric and hydrochloric acids.

Potassium Metantimonate, $2KSbO_3 + 5H_2O$, is prepared by deflagrating metallic antimony or the trisulphide with potassium nitrate. Upon lixiviation with warm water there is left a white powder, which, when boiled for some time with water, dissolves to a considerable extent.

A crystalline or a gummy mass separates from this solution, according as it is moderately or in large part evaporated.

By substituting sodium nitrate for the potassium salt, sodium metantimonate may be procured.

A basic lead metantimonate is used in oil-painting, under the name of *Naples yellow*, and is produced by heating a mixture of one part of tartar emetic, two parts of lead nitrate, and four parts of sodium chloride for two hours to the fusing point of the last-named ingredient, and subsequently washing out the soluble part with water.

Antimony Trisulphate, $Sb_2(SO_4)_3$, forms white masses of crystals as the product of the action of strong sulphuric acid on antimony or its trioxide. The compound is decomposed by water.

ANTIMONY AND SULPHUR.

Antimony Trisulphide, Sb_2S_3, **Antimonii Sulphidum,** U. S. P., occurs native as the most important ore of antimony. Though occasionally found crystallized in prisms, it usually forms columnar or striated masses, which soil the fingers like graphite. The native sulphide is purified by fusion, whereby it is separated from the associated mineral matter. The product, cr of commerce, consists of "steel-gray masses of a metallic lustre and a striated, crystalline fracture," which are easily pulverized and fused.

This article is likely to contain arsenic, which is almost completely separated by macerating the finely-divided substance with about one-half its weight of 10-per-cent. ammonium hydrate solution, which dissolves the impurity from out the antimony compound, and leaves the **Antimonii Sulphidum Purificatum,** U. S. P.

When this purified sulphide is boiled with about twelve times its weight of 5-per-cent. sodium hydrate solution for two hours, the following reaction takes place:

$$2Sb_2S_3 + 4NaOH = NaSbO_2 + 3NaSbS_2 + 2H_2O.$$

If the solution thus obtained is strained, and while still hot decomposed by excess of diluted sulphuric acid, an amorphous, reddish-brown powder is thrown down:

$$NaSbO_2 + 3NaSbS_2 + 2H_2SO_4 = 2Sb_2S_3 + 2H_2O + 2Na_2SO_4.$$

When collected, washed, and dried at a slightly elevated temperature, the powder is found to be odorless and tasteless.

It is known in medicine as sulphurated antimony, **Antimonium Sulphuratum,** U. S. P., or *kermes mineral*, and formerly was much used as a remedy.

A very small amount of trioxide contaminates the above product. Artificial trisulphides may be produced by melting antimony with sulphur, or by precipitating a solution of an antimony salt with hydrogen sulphide. The amorphous, orange, hydrated product of the last method may be changed to the crystalline black trisulphide by heat.

Uses.—Crystalline antimony trisulphide is used not only for the preparation of the other antimony compounds, but also in fireworks, such as the *blue* or *Bengal lights* used at sea, and for the preparation, especially in Sweden, of the heads of *lucifer-matches*, as well as for the composition of percussion-caps. The amorphous variety is largely used as a means for vulcanizing caoutchouc, to which it imparts a reddish-brown color.

Antimony Pentasulphide, Sb_2S_5, sometimes called *golden sulphuret of antimony*, cannot be prepared by the direct combination of its constituent elements, but can be obtained by boiling the trisulphide and sulphur with fixed alkali hydrate or carbonate and subsequent neutralization of the solution by acid.

It may also be had as a fine yellowish-red powder by aci ing a solution of a crystallized sulphantimonate. The resul precipitate, when carefully dried in the dark, is easily solub aqueous solutions of alkali hydrates and sulphides.

Antimony Cinnabar is an oxysulphide obtained by the ac of a solution of sodium thiosulphate upon antimony trichlor It is used in painting. *Crocus* and *glass of antimony* consis varying proportions of oxide and oxysulphide, and are gotte partly roasting the ore in air, or by incomplete oxidation deflagration with potassium nitrate.

Both tri- and pentasulphide of antimony are capable of c bining with the alkali sulphides to form sulphantimonites sulphantimonates respectively. Acids corresponding to t salts are not known in the free state, but the salts themse have been studied. The alkali sulphantimonites, which brown or black, are produced by fusing the alkali hydrat carbonate with antimony trisulphide, or by dissolving the la in a solution of an alkali hydrate whereby both sulphantimo and antimonite are formed. The solutions are not stable, are decomposed by acids with precipitation of the amorph trisulphide.

This class of compounds is sometimes called *liver of antim*

Sodium Sulphantimonate, $Na_3SbS_4 + 9H_2O$, or *Schlippe's S* is the best representative of the higher class of these sulpho-s It is prepared by heating a mixture of 8 parts of anhydr sodium sulphate and 3 parts of charcoal to fusion in a cr ble, and adding thereto, under continued heat, 6 parts of fin powdered antimony trisulphide previously mixed with 1½ p of sulphur, maintaining the fusion until the color of the tri phide has disappeared. The cooled mass is extracted water.

The same compound may also be made in the wet way boiling the trisulphide and sulphur with milk of lime and sod carbonate.

In both cases the filtered solutions are evaporated and allo to crystallize. The salt is obtained in fine, transparent tetr dra which are soluble in three parts of water. When the s tion is acidified antimony pentasulphide is thrown down.

Schlippe's salt is used in photography.

The sulphantimonates of the heavy metals are insoluble water, and can be formed by double decomposition of the pro substances. They include many of the ores of antimony.

Antimony Triselenide, Sb_2Se_3, and pentaselenide, Sb_2Se_5, antimony tritelluride, Sb_2Te_3, antimony phosphide, SbP, and antimony arsenide, Sb_2As_3, are known; the last as an ore of the metal, the others as products of the union of the elements.

BISMUTH.

Symbol, Bi. *Atomic Weight*, 208.9. *Valence*, III and V.

History.—Probably bismuth was first distinctly recognized in 1450 by Basil Valentine, who attempted to classify it with other metals. In the following century, Paracelsus classed it among the *semi-metals*, but it was afterwards proposed as a true metal by Agricola. Although clearly described by the last author, bismuth was subsequently confounded with other metals, especially with antimony and zinc, until 1739, when Pott contributed to the more accurate knowledge of the element. Its reactions were investigated by Bergman.

The name is from the German, *Wismuth*.

Occurrence.—The sources of bismuth are not numerous. It forms an exception to most metals by occurring chiefly in the free state, sometimes nearly pure. Both the metal and its ores are generally disseminated through rock. The most important works for its production are at Schneeberg, in Saxony, where the ore occurs associated with cobalt minerals. The mines of England, France, Hungary, and Scandinavia also afford it.

The Magnesium Works at Patricroft, in England, work up considerable quantities of imported bismuth ore, which in recent years has been brought into commerce from California, Colorado, Utah, Texas, Mexico, South America, and Australia.

Besides as native metal, bismuth is found as *bismuth-ochre*, Bi_2O_3, less frequently as *bismuthite*, Bi_2S_3, and occasionally associated with many of the heavy metals and as carbonate and silicate.

Preparation.—The process of obtaining the metal usually applied in the past consisted in heating the ore in iron tubes inclined in such a way that the easily fusible metal could run off into proper receptacles. This method extracted only that part of the bismuth which existed in the free state.

At present the ores are roasted to expel most of the sulphur, and then fused in small furnaces with iron to remove sulphur, charcoal to reduce the ore, and slag to facilitate the operation. The molten mass so obtained is allowed to stand, when a separation into two layers occurs, the lower being nearly pure bismuth.

When the upper layer, which consists of the cobalt-speiss, iron, and various constituents of the ore, has hardened, the still liquid bismuth is transferred to ingot moulds.

When the metal occurs in ores of lead and silver, it is extracted from the slag, in which it collects in quantity from 5 to 20 per cent., by cold hydrochloric acid, and subsequently precipitated as basic chloride by water, or as metal by means of iron. In all such cases it is finally reduced by soda-ash and coal.

Bismuth is generally sent into commerce in hemispherical masses which weigh from 10 to 12 kilogrammes.

Properties.—Bismuth is isomorphous with arsenic and antimony. It is generally met with in brilliant, grayish-white or iridescent masses having a crystalline lamellate texture, on account of which, although hard, the metal can be readily reduced to a powder. The roseate tinge usually present is said to arise from a slight superficial oxidation. When melted and allowed to cool the metal expands quite notably.

Bismuth is the most diamagnetic of all known bodies, a good conductor of electricity, but a poor conductor of heat. It combines directly with the halogens and sulphur, and has a specific gravity of 9.83.

It melts at 264°, and at a white heat (about 1100°) may be distilled in hydrogen. It is permanent in air at ordinary temperatures, but when heated before the blowpipe on charcoal yields bismuth trioxide as a brown incrustation, which becomes yellow on cooling.

Hydrochloric acid does not dissolve the metal, but it is soluble in nitrohydrochloric acid and in hot concentrated sulphuric acid. Nitric acid also dissolves bismuth. When an acid of specific gravity 1.2 is employed, the presence of arsenic may be detected by the white deposit of bismuth arsenate, which fails to dissolve.

Although commercial bismuth is likely to contain arsenic and other impurities, still it is usually found in the market of such purity that it can be used for preparing the compounds, particularly the basic nitrate, and some authorities state that the presence of as much as .5 per cent. of arsenic does not disqualify the metal for that purpose.

To free it of arsenic the powdered metal is mixed with 5 or 6 per cent. of potassium or sodium nitrate and fused in a Hessian crucible by means of a charcoal fire. After the half-cooled mass has been heated for a minute with 5 per cent. fixed alkali hydrate

Bismuth Trioxide, Bi_2O_3, the most important of this class of compounds, occurs naturally as *bismuth-ochre*. It may be prepared by heating bismuth or its carbonate, nitrate, or hydrate, and is usually seen in the form of a yellow, fusible powder, or as small needles of the same color.

It is insoluble in water, and constitutes a stronger base than antimony trioxide. Strong acids dissolve it to form corresponding salts of bismuth.

Bismuth trioxide is employed in the manufacture of optical glass, to which it imparts greater hardness and higher refractive power than is obtained by the use of lead.

Bismuth Dioxide, Bi_2O_2, *Bismuth Tetroxide*, Bi_2O_4, and *Bismuth Pentoxide*, Bi_2O_5, are known.

Bismuthyl Hydrate, BiO(OH), is produced when a solution of bismuth nitrate in nitric acid is slowly added to a cold solution of sodium hydrate. It is a white, amorphous powder, and has weak basic properties.

Bismuth Trihydrate, $Bi(OH)_3$.—When a solution of a bismuth salt is treated with an excess of cold ammonium hydrate, this compound is obtained as a white precipitate. It has the characters of a base, and upon heating is converted into bismuth trioxide.

Of the more acid hydrates, that having the composition $BiO_2(OH)$ is formed by passing chlorine into potassium hydrate solution in which bismuthyl hydrate has been suspended, while $Bi_2O_3(OH)_4$ is obtained by the action of potassium cyanide on bismuth nitrate.

OXYGEN SALTS OF BISMUTH.

Bismuth Nitrate, $Bi(NO_3)_3.5H_2O$, is obtained by gradually adding to 5 parts of nitric acid of specific gravity 1.2 contained in a capacious flask, and previously heated to from 75° to 90°, 1 part of coarsely-powdered bismuth. A strong reaction ensues, the metal is dissolved and nitrogen dioxide is liberated. On account of this gas changing in the air to noxious nitrogen tetroxide, the operation is best conducted in a place capable of ventilation:

$$2Bi. + 8HNO_3 = 2Bi(NO_3)_3 + 4H_2O + 2NO.$$

When the solution has been filtered through asbestos to remove bismuth arsenate, evaporated, and allowed to cool, the salt crystallizes, while the impurities remain in the mother-liquor.

Bismuth nitrate forms colorless, transparent, columnar masses which melt at 73° in their water of crystallization, and which by continued heating at 80° lose water and nitric acid, and are changed to a white basic nitrate. It dissolves in a small quantity of water to form a strongly caustic liquid, which, upon the further addition of water, is precipitated through the production of white basic nitrate, in which the proportion of the nitric acid radical is much decreased.

From this salt most of the useful salts of the metal are prepared.

Basic Bismuth Nitrate, $(BiO)NO_3.H_2O$. **Bismuthi Subnitras**, U. S. P.—This compound was introduced into the practice of medicine by Odier in 1786.

It is "a heavy, white powder, of somewhat varying chemical composition, odorless and almost tasteless, and permanent in the air. Almost insoluble in water, and insoluble in alcohol; but readily soluble in nitric and hydrochloric acids. When heated to 120° C., the salt loses water (between 3 and 5 per cent. of its weight); and when subsequently heated to redness, it evolves nitrous vapors, leaving from 79 to 82 per cent. of its weight of a yellow residue which is soluble in nitric or hydrochloric acid, and blackened by hydrogen sulphide. When brought upon moistened blue litmus paper, the salt shows a slightly acid reaction."

The composition of the salt depends upon the quantity and temperature of the water employed for precipitation and washing and the rapidity with which the process of preparation is conducted.

The official product described above may be obtained by the following method: 1 part of bismuth nitrate and 4 parts of water are thoroughly rubbed together, and the mixture during stirring is poured into 21 parts of boiling water, which react as follows:

$$Bi(NO_3)_3 + 2H_2O = (BiO)NO_3.H_2O + 2HNO_3.$$

When the precipitate has subsided, the still warm supernatant liquid is poured off, the precipitate is collected on a filter and, after the filtrate has ceased to drop, is washed with an equal volume of cold water. After a repetition of the washing, the precipitate is pressed and dried at a temperature not above 30°. On account of the acid present, the liquid from which the precipitate has been collected retains not inconsiderable amounts of bismuth nitrate, the greater part of which can be thrown down as basic nitrate, if the solution be nearly neutralized with sodium hydrate. This is usually collected, washed, and added to the first precipitate. From the filtrate the remaining traces of bismuth may be recovered as basic carbonate or as hydrate by the addition of an excess of sodium carbonate or of ammonium hydrate respectively.

100 parts of crystallized bismuth nitrate yield about 60 parts of bismuth subnitrate.

Uses.—Besides its use in medicine, bismuth subnitrate is extensively employed in cosmetics under the name of *flake-white*, and in the preparation of a colorless, iridescent glaze for porcelain and in glass staining.

Basic Bismuth Carbonate, $(BiO)_2CO_3.H_2O$. **Bismuthi Subcarbonas,** U. S. P., is "a white or pale yellowish-white powder, [illegible] chemical composition. Odorless and tastele [illegible] in air. Insoluble in water or alcohol [illegible] soluble in nitric or hydrochloric acid, with [illegible]. When heated to redness, the salt loses water [illegible] and leaves from [illegible] per cent. of [illegible] soluble in nitric or hydrochloric acid, and [illegible] hydrogen sulphide.

[illegible] by pouring a solution of bismuth nitrate into [illegible] sodium carbonate.

[illegible] carbonate is found native in small quantity [illegible] mass. Neutral bismuth carbonate is [illegible]. The commercial salt is used in medicine.

[illegible] combination with arsenic, chromic, [illegible] phosphoric, silicic, and sulphuric acids. It combines [illegible] selenium.

[illegible] salts of bismuth, with the exception of the oxy-[illegible] [illegible] yellow.

[illegible] Bi_2S_3, occurs native as *bismuthite* in Cornw [illegible] prepared by fusing bismuth with an excess [illegible] solution of a bismuth salt with hydro [illegible] bismuth are fused together in the prop [illegible] bismuth disulphide, Bi_2S_2, is obtained. [illegible] together, or hydrogen phosph [illegible] bismuth salts, produce black bismuth phosph [illegible] arsenic similarly applied give correspond [illegible] of these are unstable and of uncertain com

[illegible] considered Arsenic, Antimony, and Bism [illegible] periodic system [illegible] belong in the same gr [illegible] and Phosphorus. As supplementary to this group [illegible] we have Vanadium, Niobium [illegible] Col [illegible]

VANADIUM.

Symbol, [illegible] *Atomic Weight,* [illegible] *Valence,* III and V.

[illegible] chiefly as the vanadates of lead and copper [illegible] and other localities. It is obtained as a whitish-g [illegible] the reduction of the dichloride by hydrog [illegible] oxygen it forms five oxides correspond [illegible] The first three, or lowest of these, act [illegible] acid-forming oxides.

Vanadium Pentoxide, V_2O_5, or vanadic anhydride, is a brown m [illegible] fusing the naturally occurring vanadates with nitre. It c [illegible] with the alkalies, forming the normal *vanadates*. The free ac

H_3VO_4, is not known, but salts, such as Na_3VO_4, exist. The *metavanadic acid*, HVO_3, forms a fine yellow pigment sometimes termed "vanadium bronze." The most important salt of this acid is *ammonium metavanadate*, NH_4VO_3. The solution of this salt becomes deep black when treated with tincture of galls. As the solutions containing this highest oxide of vanadium are reduced they show very characteristic changes of color: thus, vanadic salts are yellow; hypovanadic salts blue; vanadous salts green; and hypovanadous salts lavender colored.

Vanadium forms three chlorides, VCl_4, VCl_3, and VCl_2, and a number of oxychlorides such as $VOCl_3$, $VOCl_2$, and VOCl.

NIOBIUM (or Columbium).

Symbol, Nb (or Cb). *Atomic Weight*, 93.7. *Valence*, III and V.

Niobium, as it was named by Rose, or Columbium, as it was first named by Hatchett, is a very rare metal found in columbite and tantalite and other rare minerals. Niobium has been obtained as a steel-gray crust of sp. gr. 4.06. Its most important compound is $HNbO_3$, forming salts known as *niobates*.

TANTALUM.

Symbol, Ta. *Atomic Weight*, 182. *Valence*, III and V.

Tantalum accompanies niobium in the minerals above named. It has been obtained as an iron-gray powder. Its most important compound is *tantalic acid*, $HTaO_3$, which forms *tantalates*.

CHAPTER IX.

THE CHROMIUM GROUP.

CHROMIUM.

Symbol, Cr. *Atomic Weight*, 52. *Valence*, II, IV, and VI.

CHROMIUM was discovered by Vauquelin in 1797. Klaproth, independently, and about the same time, made the same discovery. Both chemists first observed it in the mineral *crocoisite*, a lead chromate.

Chromium is not found in the free state in nature; its compounds are neither abundantly nor widely distributed. The best-known occurrence is as chrome iron ore, or ***chromite***, FeO,Cr_2O_3. This is found in the Shetland Islands, in Norway, and in the Urals. In the United States it is found near Philadelphia, in beautiful octohedral crystals, and at the chrome mines in Lancaster County, Pennsylvania. Maryland also yields some chrome ore. The chief supply in this country comes from California at the present time.

Preparation.—Chromium is obtained in the metallic state by reducing the chloride with zinc. For this purpose chromic chloride is heated in a Hessian crucible with metallic zinc, a mixture of potassium and sodium chlorides being added as a flux. The resulting metallic button is a mixture of chromium and zinc, from which the latter is dissolved by treatment with dilute nitric acid so long as anything is dissolved. The metallic chromium is left behind as a gray powder. When chromic oxide is heated to whiteness with charcoal the metal is obtained.

Properties.—Chromium, when prepared by reduction with zinc, is a light-gray, crystalline, non-magnetic powder, which is seen by the aid of a microscope to consist of minute rhombohedra. It is highly infusible, and is not easily oxidized in the air. Hydrochloric acid dissolves the metal rapidly, with evolution of hydrogen; diluted sulphuric acid, when hot, behaves in a similar manner, but concentrated nitric acid does not attack it.

Uses.—Chromium in the proportion of 0.5 to 0.75 per cent. is employed to impart hardness to steel. The United States produced in 1893 1620 tons of chrome ore, and imported 63[illegible]54 tons.

to 1 volume of a saturated solution of potassium bichromate 1½ volumes of concentrated sulphuric acid :

$$K_2Cr_2O_7 + 2H_2SO_4 = 2CrO_3 + 2KHSO_4 + H_2O.$$

By cooling, the oxide is caused to separate in acicular crystals; these are drained in a funnel, then pressed between porous bricks, again placed in the funnel and washed with nitric acid having a specific gravity of 1.46. After the nitric acid has drained off, the crystals are pressed between porous bricks a second time and dried on a sand-bath until no more nitrous fumes can be detected. Another method of purification consists in repeatedly crystallizing the chromium trioxide from a small quantity of water, and removing the last traces of sulphuric acid by the addition of a little barium chromate.

Properties.—Chromium trioxide occurs in lustrous, brownish-red, acicular crystals or rhombic prisms, having a specific gravity of 2.8. The crystals are very soluble in water, and deliquescent in moist air. The scarlet-red crystals usually contain sulphuric acid, while those that are purified from this substance are darker, with a brownish-red color and a steel-blue lustre. On account of its energetic oxidizing action the oxide cannot be brought in contact with the usual organic solvents, as they are liable to be inflamed thereby. In fact, it must be preserved in glass-stoppered bottles, and not brought in contact with such substances as cork, tannin, sugar, alcohol, etc. "When Chromic Acid is heated, its color darkens, and finally becomes black, but is restored on cooling. At 192° to 193° it fuses to a reddish-brown liquid, which, on cooling, forms a dark-red, brittle mass (often enclosing cavities filled with crystals), furnishing a scarlet powder." After protracted heating at 250° it is entirely decomposed into chromic oxide, Cr_2O_3, and oxygen.

Uses.—Chromium trioxide is employed medicinally as a caustic, in dilute solution (1 to 100) for hardening tissues in microscopic preparations, and more extensively as an oxidizing agent in the laboratory.

Chromium Oxychloride, Chromyl Chloride, CrO_2Cl_2, is obtained by introducing a fused mixture of 10 parts of common salt and 12 parts of potassium dichromate in small pieces into a retort with 30 parts of concentrated sulphuric acid. The retort must be connected with a well-cooled receiver, as the reaction proceeds without the aid of heat, a dark-red, nearly black, liquid distilling over. It has a specific gravity of 1.92 at 25°, and boils at 118°.

The potassium sulphate is used in converting another portion of calcium chromate. Potassium dichromate is purified by crystallization from five times its weight of hot water.

Potassium dichromate crystallizes in red, anhydrous, triclinic prisms or four-sided tables. It is permanent in the air, odorless, and has a bitter, metallic taste. The salt is soluble in 10 parts of cold water, in 1.5 parts of boiling water, but insoluble in alcohol. The aqueous solution is acid to litmus paper. On the application of heat it fuses without loss of weight, and at a white heat oxygen is evolved, leaving a residue of neutral potassium chromate and green chromic oxide.

Uses.—Potassium dichromate is rarely employed in medicine. It is, however, extensively used in the dyeing and tanning industries, and in a number of smaller operations.

Sodium Chromate, Na_2CrO_4, and *Dichromate*, $Na_2Cr_2O_7$, are prepared similarly to the potassium salts. The chief difficulty appears to be in the crystallization of the sodium salt. According to Walberg, the following process gives satisfactory results: 6 parts of finely-ground chrome ore (containing 44 per cent. of Cr_2O_3) are intimately mixed with 3 parts of soda-ash (containing 92 per cent. sodium carbonate) and 3 parts of chalk. The whole is strongly heated in the oxidizing flame of a reverberatory furnace, the charge of the furnace being one ton. The hot mass is lixiviated with water, forming a liquid of 84° Tw. It is then concentrated in an iron pan to 104° Tw., and run into tanks lined with lead, where acicular crystals separate, having the composition $Na_2CrO_4.10H_2O$. These are drained by a centrifugal machine, then placed in a well-ventilated chamber, heated to 30°, where they effloresce and crumble to a yellow, anhydrous powder. The dichromate is prepared from this similarly to the potassium salt. It occurs in deliquescent crystals, which are used in many technical processes in place of potassium dichromate, because of their more ready solubility in cold water.

Barium Chromate, $BaCrO_4$, is a yellow powder, insoluble in water and in acetic acid. It is obtained by precipitation of a soluble barium salt with potassium chromate or dichromate. Under the name of *yellow ultramarine* it is used as a pigment.

Lead Chromate, $PbCrO_4$.—There are at least three commercial substances which belong under this title,—namely, the neutral chromate, or *chrome yellow*, basic chromate, or *chrome red*, and *chrome orange*, which is a mixture of the two.

Chrome yellow is prepared by precipitating a solution of potassium chromate with a solution of lead acetate. The precipitate is often mixed with gypsum or barium sulphate in order to obtain the lighter chrome colors. Another process consists in digesting lead sulphate, which is a by-product in many calico-printing and dye-works, with a solution of potassium chromate. The depth of shade depends upon the amount of unchanged lead sulphate. It is stated that a beautiful chrome yellow may also be obtained by digesting 100 parts of freshly-precipitated lead chloride with 47 parts of potassium dichromate.

Chrome red is a basic lead chromate having the composition $PbCrO_4,Pb(OH)_2$. It is sometimes known as *Austrian cinnabar*. In order to obtain it the yellow chromate is boiled with a solution of potassium hydrate, or a better quality is made by fusing together equal parts of sodium and potassium nitrates, and adding to the fused mass, in small quantities at a time, the yellow chromate. After cooling, the insoluble chrome red is well washed and dried. The different shades of this compound appear to be due to the size of the crystalline particles, as may be shown by separately rubbing a number of samples to a uniform powder.

A large number of other chromates are known, and may in most cases be prepared by precipitating a soluble salt of the metal with potassium dichromate.

OXYGEN SALTS OF CHROMIUM.

Chromous Sulphate, $CrSO_4.7H_2O$, is prepared by cooling a solution of chromous acetate in dilute sulphuric acid, whereby crystals of the above composition separate. It is also obtained when metallic chromium is dissolved in dilute sulphuric acid. When concentrated sulphuric acid is added in excess to the above solution, a white salt having the composition $CrSO_4.H_2O$ is precipitated.

Chromous sulphate occurs in bluish crystals, which are isomorphous with magnesium sulphate.

Chromic Sulphate, $Cr_2(SO_4)_3.18H_2O$.—This compound is prepared by dissolving chromic hydrate in the necessary quantity of dilute sulphuric acid. The crystals may be obtained by careful evaporation or by the addition of alcohol. The solution is green when first prepared, but becomes violet on standing, and deposits crystals of a violet color.

When the violet-colored solution is boiled for some time it becomes green, and is then not precipitated by alcohol, and yields an amorphous, green mass by evaporation; but by long standing the solution again becomes violet, and will then yield the normal salt either by evaporation or by precipitation with alcohol.

It is probable that the boiling causes the formation of a basic salt.

Chromium and Potassium Sulphate, $K_2Cr_2(SO_4)_4.24H_2O$, *Chrome Alum*.—This salt is obtained by dissolving in water molecular proportions of chromic sulphate and potassium sulphate and carefully evaporating. The violet-red solution yields dark crystals of the same color as the solution from which they separate, having the above composition. It may also be prepared by adding to an aqueous solution of potassium dichromate the necessary quantity of sulphuric acid and passing in sulphurous oxide. When the solution is heated it turns green, and crystals cannot be obtained from it, but by long standing it acquires the violet-red color and will then crystallize.

Other alums of chromium may be obtained by the substitution of the sulphates of ammonium or sodium.

Chrome alum is obtained commercially as a by-product in the manufacture of certain aniline dyes. It is used as a mordant in dyeing, and to some extent in the manufacture of leather.

Chromic Nitrate, $Cr_2(SO_4)_3.18H_2O$, is obtained by dissolving chromic hydrate in nitric acid. The resulting solution is blue by transmitted light and red by reflected light, and the crystals which are deposited have a purple-red color.

Chromic Phosphate, $Cr_2(PO_4)_2$, is made by adding to chromic chloride a solution of sodium phosphate. It is obtained as a green precipitate, which becomes blue on drying.

CHROMIUM AND SULPHUR.

Chromium Sesquisulphide, Cr_2S_3, is prepared by passing hydrogen sulphide over heated chromic chloride or chromium trioxide. It may also be obtained by the direct union of metallic chromium and sulphur. It is a grayish-black mass.

Chromium Monosulphide, CrS, is said to have been found in meteoric iron, and it is claimed that *Chromium Persulphide*, Cr_2S_7, is formed when hydrogen sulphide is passed into a solution of potassium dichromate in water of ammonia.

MANGANESE.

Symbol, Mn. *Atomic Weight*, 54.8. *Valence*, II, IV, and VI.

History.—The ore called *pyrolusite*, or black oxide of manganese, was known to the early chemists, by whom it was confounded with magnetic oxide of iron or magnetite.

In 1740, Pott showed that this mineral did not contain iron, and, in 1774, Scheele recognized it as very different from the ores of iron, and further investigated it.

The metal was first separated by Gahn, in the same year, and later, in larger quantities, by St. Claire-Deville and Brunner.

The name manganese is supposed to have been given the new element to distinguish it from magnesia.

Occurrence.—Manganese occurs in nature as a frequent associate of iron, to which by its properties it is closely related. It exists free to a small extent in meteoric iron.

The most widely-occurring ores are the oxides, of which the most important is manganese dioxide, or *pyrolusite*, MnO_2. Besides this it is found as sesquioxide, or *braunite*, Mn_2O_3, as

MANGANESE AND THE HALOGENS.

Manganous Chloride, $MnCl_2.4H_2O$.—This is obtained as a side product in the preparation of chlorine from manganese dioxide and hydrochloric acid. In the residual liquid it is mixed with iron, from which to separate it the filtered liquid is evaporated to dryness to expel free acid, the residue treated with water, and the resulting solution heated with an excess of manganous carbonate. After filtration the solution is evaporated and allowed to crystallize. The manganous carbonate required for the operation is previously prepared from some of the iron containing liquid by precipitation with sodium carbonate. Should lead and copper be present, they are precipitated by hydrogen sulphide after the iron has been separated and before the solution is concentrated for crystallization. It is a pink, deliquescent salt.

Manganic Chloride, Mn_2Cl_6, and *Manganese Tetrachloride*, $MnCl_4$, have never been isolated, for they readily decompose, giving chlorine and manganous chloride.

Manganous Bromide, $MnBr_2.4H_2O$, and *Manganous Iodide*, $MnI_2.4H_2O$, are pink, deliquescent salts obtained by dissolving manganous carbonate in hydrobromic or hydriodic acid.

MANGANESE AND OXYGEN.

Manganous Oxide, MnO, is obtained as a green powder by heating manganous carbonate, or an oxide of manganese that is richer in oxygen, in a stream of hydrogen. It is a strong base, and dissolves easily in acids with the formation of manganous salts.

Manganous Hydrate, $Mn(OH)_2$.—Manganous oxide forms a hydrate of an unstable character, as a white, flocculent precipitate when a solution of a manganous salt is decomposed by potassium or sodium hydrate. It is insoluble in excess of either precipitant, but is soluble in ammonium hydrate. It soon acquires in the air a brown color, due to partial change to manganic hydrate, which is insoluble in all the alkali hydrates.

Manganese Sesquioxide, Mn_2O_3, occurs in nature as braunite crystallized in brown-black, lustrous, very hard, obtuse quadratic pyramids. It is usually prepared and of the same color by careful ignition of manganous hydrate, manganese dioxide, or manganic nitrate. It is a very weak base, in consequence of which it combines with acids only with difficulty.

Hot hydrochloric acid effects solution with liberation of chlorine and production of manganous chloride.

Manganic Hydrate, $Mn_2(OH)_6$.—As mentioned above, this compound results from the oxidation of manganous hydrate, and is prepared by allowing that change to take place. In cold hydrochloric acid it dissolves to a dark-brown liquid, which is considered to contain manganic chloride, the instability of which is shown by its decomposition into manganous chloride and chlorine when the solution is gently warmed. It is used in the preparation of varnishes.

The mineral manganite has the composition $Mn_2O_3.H_2O$.

Manganoso-manganic Oxide, Mn_3O_4, occurs native as hausmannite in brown-black quadratic pyramids. It results upon the continued ignition of the oxides of manganese, of the hydrates, and of the carbonate with access of air. With evolution of chlorine it dissolves in hydrochloric acid to yield manganous chloride.

Manganese Dioxide, MnO_2. **Mangani Dioxidum,** U. S. P.—This most important of manganese ores was known and used in the Middle Ages. It is often called black oxide of manganese or pyrolusite. The largest deposits are in the Russian Caucasus, Chili, Cuba, Germany, France, and in the United States in Virginia, Arkansas, and Colorado. It crystallizes in steel-gray, more or less lustrous, rhombic masses, which usually enter commerce in a compact or striated state. The dioxide can be artificially prepared by carefully heating manganous oxide with potassium chlorate, or by repeated treatment of manganous oxide with hot concentrated nitric acid, or by moderate heating of the corresponding hydrate.

From the manganous chloride residues left upon making chlorine the manganese is recovered by Weldon's process, which depends upon the formation of dioxide when air is blown through the residue mixed with milk of lime. Upon paper or porcelain it gives a gray-black streak, and when crushed a graphite-colored powder. The other oxides give brown stains and powders. The specific gravity of the mineral varies between 4.7 and 5.1. It is not attacked by water, nitric acid, or dilute sulphuric acid. When heated with strong sulphuric acid to 100° it gives manganic sulphate, while at 200°, manganous sulphate results. In the presence of easily oxidizable organic substances, such as sugar or oxalic acid, it dissolves in dilute sulphuric acid with liberation of oxygen, which acts upon the organic matter present.

Hydrochloric acid yields with the dioxide chlorine and manganous chloride. At a low red heat it gives off one-fourth of its oxygen and changes to sesquioxide, while at a higher temperature it gives up one-third, and passes into manganoso-manganic oxide. The pyrolusite of commerce is not pure, but contains, besides other oxides of manganese, variable quantities of calcium and barium carbonates and sulphates, silica, and iron oxides. The official requirement is the native compound containing at least 66 per cent. of pure dioxide, estimated by the amount of ferrous sulphate that is oxidized when that substance is boiled with the sample and hydrochloric acid. With some basic oxides manganese dioxide forms salts known as manganites. The acid corresponding to these compounds is not recognized in the free state.

Uses.—Manganese dioxide serves for the preparation of other manganese compounds, of oxygen, of chlorine, and for the decolorization of glass, in which it corrects the green color imparted by the iron oxide derived from the sand used. Aside from the last use, it is employed to give an amethyst color to glass.

Manganic Anhydride, MnO_3, has not yet been prepared, nor is the corresponding hydrate, or manganic acid, H_2MnO_4, known in the free state. The salts of the acid, however, are well known under the name of manganates.

Potassium Manganate, K_2MnO_4.—This compound is made by evaporating 100 parts of potash lye of specific gravity 1.33 in a bright iron kettle to about one-third its weight, and adding to the fused potassium hydrate so obtained 30 parts of manganese dioxide and 28 parts of potassium chlorate, separately powdered and previously mixed on a sheet of paper. The mass is then dried with constant stirring to a stiff consistency, and then heated in a Hessian crucible to a low red heat until a small quantity taken out and put into water almost completely dissolves with an intense green color:

$$3MnO_2 + 6KOH + KClO_3 = 3K_2MnO_4 + KCl + 3H_2O.$$

The heating of the mixture must not be carried to full fusion, or decomposition of the manganate ensues. When the reaction has been shown to be complete, the mass is poured out on an iron plate, and, when cold, is broken and extracted with water. The solution is filtered through asbestos, and then evaporated in a rarefied atmosphere, whereby the salt is obtained in dark-green, almost black crystals.

In both cases a precipitate of hydrated dioxide is produced.

After standing, the clear solution is siphoned off, and the last turbid portion is filtered through asbestos. Care having been taken to exclude dust, the liquid is evaporated until a pellicle forms on the surface, and then allowed to cool. The crystals which separate are collected and placed to drain out of contact with organic matter. The salt may be obtained in a crude state by evaporating the solution at once to dryness. It forms metallic, lustrous, almost black, rhombic prisms, which are permanent in the air. These are soluble in 16 parts of water at 15°, and in 3 parts of boiling water. The solution gradually undergoes change. Potassium permanganate is a powerful oxidizing agent toward organic and inorganic substances. In neutral solution one molecule of the salt gives up three atoms of oxygen, with the production of a brown, flocculent precipitate of a hydrated dioxide.

In acid solution one molecule gives up five atoms, and if sufficient of the oxidizable matter is present, a clear and colorless solution results. On account of the ease with which they yield their oxygen, both manganate and permanganate are employed as disinfectants: foul-smelling gases or substances are rendered entirely odorless by contact with these compounds. Its use in the quantitative analysis of iron and of organic matter in potable waters depends upon this same feature. Chlorine is liberated by the action of hydrochloric acid on potassium permanganate. The salt is occasionally used in the practice of medicine.

Sodium Permanganate, $Na_2Mn_2O_8.6H_2O$, is prepared by a method similar to that used for making the potassium salt. It is a very hygroscopic, and therefore difficultly crystallizable, substance.

Ammonium Permanganate, $(NH_4)_2Mn_2O_8$, is isomorphous with the potassium compound. It results upon the double decomposition of molecular quantities of barium permanganate and ammonium sulphate, or of silver permanganate and ammonium chloride. It is easily decomposed by heat.

Barium Permanganate, $BaMn_2O_8$, forms needle-shaped, almost black crystals, and is gotten by the action of carbon dioxide on barium manganate suspended in water, or by reacting on silver permanganate with barium chloride.

Zinc Permanganate, $ZnMn_2O_8$, as easily-decomposable, deep dark-red, lustrous crystals, is prepared by decomposition of barium permanganate by the proper amount of zinc sulphate, or of silver permanganate by zinc chloride, and evaporation of the supernatant liquid *in vacuo*.

Permanganic Acid, $H_2Mn_2O_8$, is known only in aqueous solution. It may be made by the action of dilute sulphuric acid on barium permanganate, or by boiling a manganese compound that is free from chlorine with nitric acid in the presence of red oxide of lead. The production of its rose-red color by the last method is used as a test for manganese under the name of Crum's process.

Permanganic Anhydride, Mn_2O_7, is the oxide which corresponds to permanganic acid. As a heavy, greenish-black, readily decomposing liquid, it is produced when potassium permanganate is added in small quantity to well-cooled concentrated sulphuric acid.

The greatest care should be exercised in the application of these substances as oxidizing agents, as explosion is likely to occur if the action is sudden.

MANGANESE AND SULPHUR.

Two sulphides of manganese are found native. Manganese monosulphide, MnS, occurs as *manganese-blende* in black, cubic crystals, and manganese disulphide, MnS_2, as *hauerite* in red-brown crystals of the same system.

The former sulphide may be prepared as a green powder by heating manganese sesquioxide in a stream of hydrogen sulphide, or by precipitating a solution of a manganous salt with an alkali sulphide, whereby a flesh-pink precipitate of a hydrated sulphide is thrown down. Upon exposure to air, this takes up oxygen and assumes a brown color.

OXYGEN SALTS OF MANGANESE.

Manganous Sulphate, $MnSO_4.4H_2O$. **Mangani Sulphas, U. S. P.**—This salt is prepared by rubbing a convenient quantity of finely-powdered dioxide of good quality to a thick paste with concentrated sulphuric acid, then heating the mixture in a Hessian crucible by a blast-furnace gradually to low redness, and maintaining that condition as long as white fumes of sulphur trioxide are evolved:

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

From time to time a portion of the mass is taken out, allowed to cool, and treated with water. The solution is then filtered and tested for iron, which, if found, necessitates heating the materials to full redness, until after another trial the water solution is found to be destitute, or nearly so, of iron.

The gray-white mass is allowed to cool, and is then powdered and extracted with three times its weight of hot water, which, by frequent stirring, dissolves the salt.

Most, if not all, of the iron is left undissolved as oxide. Any traces remaining in solution are removed by manganous carbonate, which precipitates the impurity as hydrate. The filtered, iron-free solution is slowly evaporated at a low temperature.

Lead and copper are removed by saturating the liquid with hydrogen sulphide previous to evaporation, while zinc is separated by the same reagent, but in the presence of sodium acetate and acetic acid.

Manganese sulphate forms pale, rose-colored crystals which are somewhat efflorescent, and the amount of whose water of crystallization and whose crystalline form vary according to the temperature at which the crystals separate. Besides that of official composition which contains four molecules of water of crystallization, and which is obtained in rhombic prisms between 20° and 30°, monoclinic crystals having the formula $MnSO_4.7H_2O$ can be produced below 6°. They are isomorphous with ferrous sulphate. Between 7° and 20° a salt of the composition $MnSO_4.5H_2O$ crystallizes in the triclinic system, which also includes copper sulphate. When the solution is evaporated at a temperature above 30°, an almost colorless, difficultly soluble, crystalline powder of still lower percentage of water separates.

The official salt is soluble in an equal weight of water to produce a neutral solution. It is not soluble in alcohol. With the sulphates of potassium and sodium, manganese sulphate gives crystalline monoclinic double salts. Manganous sulphate finds a limited use in medicine.

Manganic Sulphate, $Mn_2(SO_4)_3$, is a dark-green, deliquescent powder which results from the action of concentrated sulphuric acid on manganese sesquioxide or on the dioxide at from 100° to 140°.

Manganese alums crystallize in octohedra, and arise from the union of the alkali sulphates with manganic sulphate.

Manganous Nitrate, $Mn(NO_3)_2.6H_2O$, separates in deliquescent crystals when manganese carbonate is added to nitric acid and the solution is evaporated.

Manganous Phosphate, $Mn_3(PO_4)_2.7H_2O$, is produced as a white precipitate by the addition of sodium phosphate to a solution of manganous sulphate.

Manganese Borate is formed when a solution of a manganous salt is precipitated by sodium borate. The white precipitate thrown down becomes brownish upon drying.

Manganous Carbonate, $MnCO_3$.—Manganese-spar, the native form of this compound, occurs in red, hexagonal crystals, which are contaminated with iron and other carbonates. The artificial white salt is prepared by adding a slight excess of sodium carbonate to a solution of manganous sulphate. Upon drying it undergoes some decomposition and becomes darker on account of the sesquioxide formed. When ignited it loses carbon dioxide and leaves manganoso-manganic oxide.

Manganic Phosphate, $Mn_2(PO_4)_2.2H_2O$, consists of a greenish-gray powder, which is obtained by the gradual addition of a concentrated solution of manganous nitrate to a 25 per cent. solution of phosphoric acid previously heated to and subsequently maintained at 100°. Dilute nitric or sulphuric acid does not alter it, but concentrated hydrochloric acid dissolves it, chlorine being set free.

Manganic Arsenate, $Mn_2(AsO_4)_2.2H_2O$, can be prepared in the same manner as is the manganic phosphate. It is a gray powder.

MOLYBDENUM, TUNGSTEN, URANIUM.

In addition to chromium and manganese, in the foregoing group we have the rarer elements molybdenum, tungsten, and uranium.

The whole group possesses many points of resemblance to the sulphur group of non-metals. The members have an equivalence II, IV, VI, and some of them more rarely VIII.

Molybdenum, Mo. *Atomic Weight*, 95.9.—This element occurs in nature chiefly as *molybdenite*, MoS_2, and as *wulfenite*, a lead molybdate, $PbMoO_4$. It is more rarely found as the trioxide, MoO_3.

Molybdenum is prepared by heating the chloride or oxide to a high temperature in a current of hydrogen. It is a silver-white, infusible metal, harder than topaz, and having a specific gravity of 8.6. It is permanent in the air, unless heated, when it is slowly converted into the trioxide. Hydrochloric, hydrofluoric, and dilute sulphuric acids do not dissolve it, but it is readily attacked by nitric acid and nitro-hydrochloric acid.

Molybdenum Pentachloride, $MoCl_5$, is formed by gently heating the metal in a current of chlorine. The *trichloride* is prepared from this by heating to 250° in a current of hydrogen. The *dichloride* and *tetrachloride* are also known.

Molybdenum Trioxide, MoO_3, is the final product of the oxidation of the metal. The other oxides are prepared from this by various processes of reduction. They are MoO_2, Mo_2O_3, and MoO.

Molybdic Acid is a term applied to the trioxide, and its combinations with various bases are known as molybdates.

Ammonium Molybdate, $(NH_4)_2MoO_4$, is formed by dissolving molybdenum trioxide in solution of ammonia, and precipitating the salt formed by the addition of alcohol.

Phosphomolybdic Acid is prepared by the union of phosphoric and molybdic acids.

The one richest in molybdenum, obtained by evaporating an aqueous solution of these two acids, has the composition $2H_3PO_4,24MoO_3.58H_2O$. It occurs in yellow crystals, and loses water at 140°.

Ammonium Phosphomolybdate, $11(MoO_3),(NH_4)_3PO_4.6H_2O$, is the compound which is formed when ammonium molybdate in the presence of nitric acid is added to phosphoric acid or a phosphate.

Tungsten (Wolfram), W, *Atomic Weight*, 183.6, is found in nature as *wolframite*, an iron and manganese tungstate. Like molybdenum, it forms a great number of compounds, and as *tungstic acid* combines with bases to form a great variety of salts.

Uranium, U, *Atomic Weight*, 238.8, occurs in nature chiefly as the mineral *uranite*, or *pitch-blende*, U_3O_8. It has many characters in common with molybdenum and tungsten, but possesses more basic properties. The metal is not so permanent, and ignites when heated with access of air to 170°. It has a specific gravity of 18.4.

Three chlorides of uranium are known, as follows: the *trichloride*, UCl_3, the *tetrachloride*, UCl_4, and the *pentachloride*, UCl_5.

The *dioxide*, UO_2, and the *trioxide*, UO_3, are known; the latter is basic towards acids, and forms salts containing the bivalent radical *uranyl*, UO_2. The uranyl salts are yellow, and impart to glass when fused with it a remarkable fluorescence.

Uranyl Chloride, UO_2Cl_2, is formed by heating the dioxide to redness in a current of chlorine.

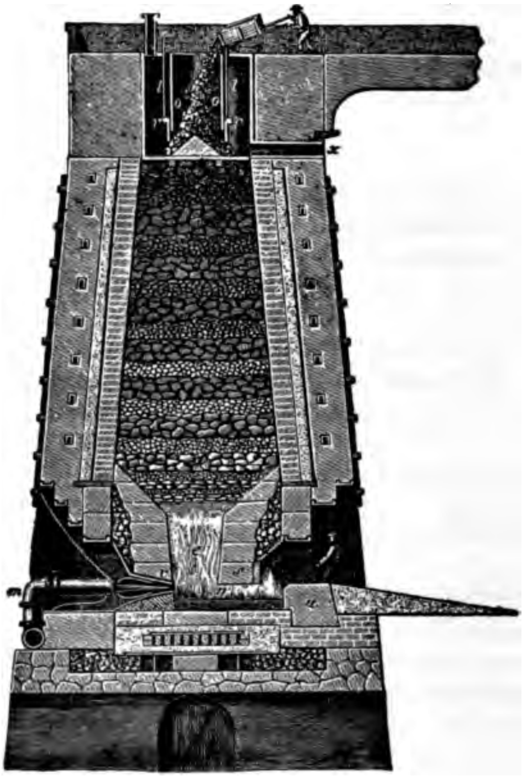
Uranium Pentoxide, U_2O_5, is a black powder used for painting black on porcelain.

Green Oxide of Uranium, U_3O_8, is formed by heating UO_2 or UO_3 in oxygen.

commercial varieties, differing in both physical and chemical characters,—viz., cast-iron, wrought-iron, and steel. According to the present method of working the ores, cast-iron is the first variety obtained.

Cast-iron.—While the earliest processes for the manufacture of iron allowed of the production of a relatively pure iron direct from the ore, such production was wasteful and expensive. The ore is now first submitted to the blast-furnace treatment, and the product is an iron containing from 3 to 6 per cent. of carbon, together with smaller amounts of other elements, such as silicon and phosphorus, and, it may be, manganese. The theory of the blast-furnace may be readily understood from Fig. 87. A tall, cylindrical or conical chamber, lined with fire-brick, is filled with

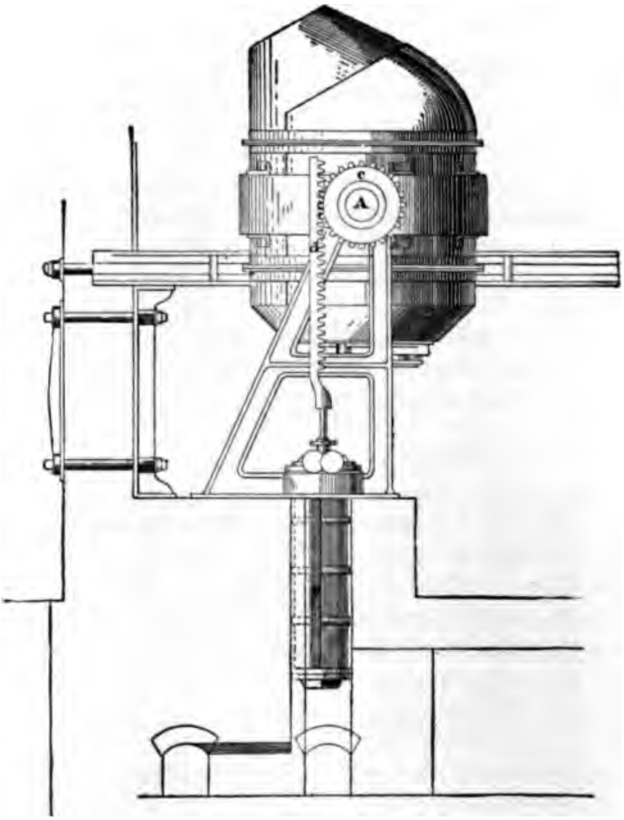
FIG. 87.



Sectional view of blast-furnace.

ing-point. The first method, and for a time the only one, was the "cementation process." In this the bars of wrought-iron cut in short lengths are packed with fine charcoal in fire-clay chests or "troughs," and heated to about 1100° for from 4 to 8 days, when the bars are found to be converted into hard steel, known as *blister steel.* This is then frequently melted in plumbago crucibles at a white heat and cast into ingots known *crucible steel,* which is the hardest and finest variety, and is us for edged tools and temper steel. The second method of ste making is the Bessemer process, which, as has well been said, the greatest metallurgical discovery that has ever been made. I this we start with cast-iron, of which some 4 to 10 tons are melted

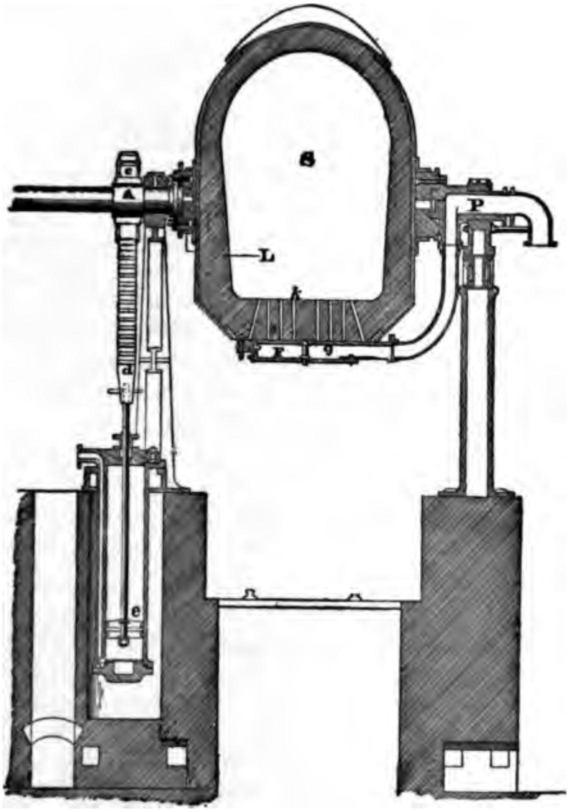
FIG. 88.



Bessemer converter.

in one charge in a vessel known as the "converter," and a powerful blast of air is blown through the molten metal until the necessary amount of carbon has been burned out. The Bessemer converter is shown in Fig. 88 in general view, and in Fig. 89 in section. The converter, which is lined with fire-brick, is first heated to a bright, red heat and put into a horizontal position.

FIG. 89.



Sectional view of Bessemer converter.

The pig-iron is then run in from a cupola, or it may be direct from the blast-furnace, and the blast turned on when the converter is swung back into a vertical position. The reaction lasts some 20 minutes, and is known to be complete by the change in the appearance of the flame that issues from the mouth of the converter. In this time the carbon of the cast-iron is almost entirely burned out, leaving what might be called a wrought-iron. The converter is, therefore, returned to the horizontal position, the blast is shut off, and a certain quantity (some 7 per cent.) of spiegel-iron, rich in carbon and manganese, is added to the charge, which gives to the iron the quantity of carbon necessary for its transformation into steel, while the manganese reduces what oxide of iron has formed in the molten mass. The third process for the manufacture of steel is the "open-hearth" or Siemens-Martin process. In this is taken either a mixture of pig-iron and ore, which is heated with a reverberatory flame, as in the puddling process, or bars and blooms of wrought-iron are heated with the pig-iron, and steel is made by the combination of the two. The steel so obtained is run, while in the molten state, through suitable channels into ingot moulds to solidify.

Steel contains 0.8 to 1.5 per cent. of carbon, all of which is chemically combined with the iron. Its specific gravity is 7.6–8.0. It has a fine-grained structure, and melts at about 1400°. If cooled rapidly it becomes hard and brittle; if cooled slowly it is soft, and may be forged and welded. Steel is tempered by reheating it to temperatures varying from 220° to 320°, according to the use intended, and then allowing it to cool slowly. It thus acquires elasticity combined with hardness.

The entire production of pig-iron throughout the world in 1892 amounted to 26,859,554 metric tons, of which the United States produced 9,304,428 tons; the world's production of steel for the same year was 12,019,114 metric tons, of which the United States produced 4,235,541 tons.

Properties.—The purest of the commercial varieties just mentioned is wrought-iron. Accordingly this is taken as the official iron of the Pharmacopœia (**Ferrum,** U. S. P.), and is described as "metallic iron in the form of fine bright and non-elastic wire." Its other characters have been given under wrought-iron. Another form of the metal recognized officially is *reduced iron* (**Ferrum Reductum,** U. S. P.). This is iron reduced from the sesqui-oxide by hydrogen. The oxide is directed to be prepared by the U. S. Pharmacopœia of 1870 by calcining the thoroughly-washed subcarbonate. The reduced iron forms an iron-gray powder without metallic lustre, readily oxidizing on exposure to air, and liable to contain some oxide of iron from imperfect reduction or after oxidation.

Ferric Iodide, Fe_2I_6, may be prepared by heating iron filings with an excess of iodine, but is unstable, and decomposes on cooling into ferrous iodide and free iodine.

Both *Ferrous Fluoride*, FeF_2, and *Ferric Fluoride*, Fe_2F_6, have been obtained, and are relatively stable. The former may be had crystallized with 8 molecules of H_2O in greenish prisms, and the latter in colorless crystals with 9 molecules of H_2O.

IRON AND OXYGEN.

Ferrous Oxide, FeO, is obtained as a black powder either by reducing ferric oxide with carbon monoxide or by heating ferric oxide to 300° and passing hydrogen over it. It readily oxidizes, and when prepared by this latter method becomes incandescent on exposure to the air, so rapid is the oxidation.

Ferrous Hydrate, $Fe(OH_2)$, is thrown out of ferrous solutions by the alkalies as a greenish-white precipitate. It soon absorbs oxygen, and changes first to a dirty green and then to a reddish brown. Ferrous hydrate is also formed by the action of pure water containing air in solution on iron. It dissolves in about 150,000 parts of water with an alkaline reaction.

Ferric Oxide, Fe_2O_3, is found abundantly in nature as red hematite or specular iron. Artificially it is prepared by igniting the hydrate or any ferric salt containing a volatile acid, forming what looks at first like a steel-gray powder, but which, when finely ground, takes a brownish-red color. It is also obtained on a large scale, when fuming sulphuric (or Nordhausen) acid is distilled from green vitriol, as a dark-red powder under the name of "colcothar" or *caput mortuum*, and is used as polishing-powder and as a basis of paints. Natural ochres also furnish an oxide which, after ignition, proves valuable for use as a pigment.

Ferric Hydrate, $Fe_2(OH)_6$ (**Ferri Oxidum Hydratum**, U. S. P.), is formed when a ferric solution is precipitated by adding an excess of ammonia. It appears as "a brownish-red magma, wholly soluble in hydrochloric acid without effervescence." On boiling it becomes more compact, gives up water, and is converted into the hydrate $Fe_2O(OH)_4$ (or $Fe_2O_3 + 2H_2O$). The same change takes place gradually by the prolonged contact of the precipitated hydrate with water, and ultimately a bright-red amorphous powder of the composition $Fe_2O_2(OH)_2$ (or $Fe_2O_3 + H_2O$) remains. Neither of these lower hydrates is as efficient an arsenic antidote as the freshly-precipitated ferric hydrate. Freshly-precipitated ferric hydrate is soluble in solution of ferric chloride with dark-red color owing to the formation of a basic chloride. If this solution be allowed to dialyze we can obtain a liquid containing 98.5 per cent. of ferric hydrate and 1.5 per cent. of hydrochloric acid. These solutions are known as "Dialyzed Iron."

Ferroso-ferric Oxide, Fe_3O_4 (or $FeO.Fe_2O_3$).—This combination of the two oxides of iron is found abundantly in nature as the magnetic or black oxide of iron. It is also formed when iron is quickly burned in oxygen or when steam is passed over ignited iron. The iron scale that forms when wrought-iron is heated in the air is a varying mixture of ferrous and ferric oxides.

Similar combinations of ferric oxide with other protoxides occur in nature as the mineral *Franklinite* (containing zinc oxide with ferric oxide), while in *Chromite* (or chromic iron) we find chromium sesquioxide with ferrous oxide in combination.

Ferric Acid.—When iron filings are fused with nitre we obtain a cherry-red fused mass from which water dissolves out *potassium ferrate*, K_2FeO_4. This compound may be obtained in crystals isomorphous with potassium chromate and sulphate. It is, however, unstable and soon decomposes. The free acid, H_2FeO_4, has not been obtained.

OXYGEN SALTS OF IRON.

Ferrous Sulphate, $FeSO_4.7H_2O$ (**Ferri Sulphas**, U. S. P.), has long been known under the name of *green vitriol*. It forms "large, pale bluish-green, monoclinic crystals, without odor, and with a saline, styptic taste; efflorescent in dry air." In moist air, the crystals rapidly absorb oxygen and become coated with a brownish-yellow crust of basic ferric sulphate. It is readily soluble in water, insoluble in alcohol. The aqueous solution of the salt has an acid reaction. When heated the salt loses 6 molecules of water at 100° and the seventh only at 300°. The official dried ferrous sulphate (**Ferri Sulphas Exsiccatus**, U. S. P.) is stated to have approximately the composition $2FeSO_4.3H_2O$, and forms a grayish-white powder. The official granulated salt (**Ferri Sulphas Granulatus**, U. S. P.) has the same composition, $FeSO_4.7H_2O$, as the crystals, but is got in crystalline powder by allowing the clear aqueous solution to run into alcohol, in which the salt is insoluble.

Ferrous sulphate forms crystallizable double salts with alkali sulphates, as $FeSO_4.(NH_4)_2SO_4.6H_2O$. As these double salts are more stable than the ferrous sulphate by itself and oxidize only slowly in the air, they are often used in the laboratory.

Ferric Sulphate, $Fe_2(SO_4)_3$, forms a white mass which gradually dissolves in water with a reddish-brown color. The solution is official as **Liquor Ferri Tersulphatis,** U. S. P. Ferric sulphate unites with alkali sulphates to form iron alums. Of these, the ammonium alum, $Fe_2(SO_4)_3(NH_4)_2SO_4.24H_2O$, is official as **Ferri et Ammonii Sulphas,** U. S. P. It crystallizes in "pale violet, octohedral crystals, without odor, and having an acid, styptic taste; efflorescent on exposure to the air." It is soluble in water, insoluble in alcohol.

A basic or subsulphate of iron is also official in solution as **Liquor Ferri Subsulphatis,** U. S. P., known commonly as *Monsel's Solution.* In its preparation, the ferrous sulphate taken is converted into ferric sulphate at the expense of the nitric acid added; but the sulphuric acid mixed with the nitric is in quantity insufficient to form the normal salt. The formula assigned to the salt contained in this solution is $Fe_4O(SO_4)_5$, or according to other authorities $Fe_2(SO_4)_3 5Fe_2O_3.H_2O$.

Ferric Nitrate, $Fe_2(NO_3)_6$, is formed when iron is dissolved in nitric acid. It crystallizes either with 12 molecules of water in cubes or with 18 molecules in monoclinic crystals, both forms being colorless and deliquescent. A solution of the ferric nitrate is official as **Liquor Ferri Nitratis,** U. S. P.

Ferrous Phosphate, $Fe_3(PO_4)_2.8H_2O$, occurs as the mineral *vivianite* in bluish monoclinic prisms. Obtained artificially it is a white, amorphous powder, which speedily oxidizes in the air.

Ferric Phosphate, $Fe_2(PO_4)_2$, is obtained as a white precipitate on adding sodium phosphate to ferric solutions. It is present in the official scale preparation **Ferri Phosphas Solubilis,** U. S. P.

Ferric Pyrophosphate, $Fe_4(P_2O_7)_3$, is the salt present in **Ferri Pyrophosphas Solubilis,** U. S. P., another scale preparation.

Ferric Hypophosphite, $Fe_2(PH_2O_2)_6$, **Ferri Hypophosphis,** U. S. P., forms "a white or grayish-white powder, odorless and nearly tasteless; permanent in the air." Like other hypophosphites it is readily oxidized by oxidizing agents.

Ferrous Carbonate, $FeCO_3$, occurs in nature as the mineral *siderite* or *spathic iron.* It is artificially obtained by adding sodium carbonate to ferrous solutions, forming a white precipitate which rapidly oxidizes in the air to ferric hydrate. The official preparation **Ferri Carbonas Saccharatus,** U. S. P., protects the carbonate by admixture with sugar. Ferrous carbonate is slightly soluble in water containing dissolved carbon dioxide, and hence is present in the natural chalybeate mineral waters.

Potassium Ferrocyanide and *Ferricyanide* are described later under the cyanogen compounds in Part IV.

Most of the Canadian ore, however, is smelted and reduced to metal in the United States.

Preparation and Properties.—Such nickel ores as contain sulphur or arsenic are first roasted, and the product, known as "speiss," is then dissolved in hydrochloric acid, and the separation of nickel from the accompanying metals accomplished in the wet way. The New Caledonian ore, being free from arsenic, sulphur, and cobalt, is smelted in a blast-furnace very much like iron ores, or it may be at once treated with hydrochloric acid, and the solution of nickel salt then precipitated with oxalic acid and the oxalate reduced to metal with lime and carbon.

Nickel is a lustrous white metal with a steel-gray tinge. Its specific gravity is 8.9. When pure it is malleable, and can be welded. The cast-nickel formerly obtained from arsenide and sulphide ores did not possess these properties, owing to the combined carbon, which made it like cast-iron. In 1879, Fleitmann discovered that the addition of ⅛ of 1 per cent. of magnesium rendered the nickel malleable and more fusible. Since then it has been found that manganese in amount from 2 to 5 per cent. would accomplish the same result. The purest nickel has been made by Mond, who takes up the metal in a gaseous compound by passing carbon monoxide over it at a moderate heat, and then at a higher temperature decomposes the compound, separating pure metallic nickel.

Uses of the Metal.—Nickel has long been used in admixture with copper and zinc in the manufacture of German silver; it has also been used with copper alone in coinage alloys, and within the last few years in the manufacture of nickel-steel armor-plate, which has produced a great increase in the demand for the metal. Nickel-plating has also been an important utilization of the metal, as the coating, if well deposited, undergoes scarcely any oxidation, and takes a high polish. The solution from which the plating is done is always that of the nickel-ammonium sulphate.

Nickel Compounds.—Nickel, like iron, forms two well-defined series of salts: the *nickelous* compounds, in which it has the valence two, and the *nickelic*, in which the double atom Ni_2 acts as a hexad group. The former series appear to be the more stable.

Nickelous Chloride, $NiCl_2.6H_2O$, forms green monoclinic prisms, soluble in water and alcohol. When heated they lose water, and when anhydrous show a yellow color.

Nickelous Cyanide, $Ni(CN)_2$, is an apple-green precipitate easily soluble in excess of potassium cyanide, with the formation of a crystalline the accompanying metals is effected by the use of bleaching-powder, which precipitates the cobaltic hydrate.

Cobalt is a slightly reddish-white metal, harder than iron, and of specific gravity 8.5–8.7. It is attracted by magnets, but in a lesser degree than iron. It is slowly attacked by sulphuric and hydrochloric acids, more readily by nitric acid. Cobalt is somewhat used for plating upon other metals, like nickel, but most of it is made into the oxide for use in the manufacture of the pigment *smalt*. The total annual production of cobalt is about 200 tons.

Compounds of Cobalt.—Two well-defined series of compounds are formed here also: the *cobaltous* and the *cobaltic*, corresponding to the ferrous and the ferric. The former of these possess a reddish color when in the hydrated state, but become blue when made anhydrous.

Cobaltous Chloride, $CoCl_2$, is obtained by the solution of cobaltous oxide in hydrochloric acid. It forms red, prismatic crystals which dissolve, yielding a pale pinkish solution. This is well known as the basis of "sympathetic inks;" these leave upon paper almost invisible characters, which when sharply dried become blue.

Cobaltous Oxide, CoO, is obtained as a green powder on heating out of contact with air the cobaltous hydrate.

Cobaltous Hydrate, $Co(OH)_2$, is obtained as a rose-red precipitate on the addition of alkalies to hot cobaltous solutions. In cold solutions a blue basic salt is precipitated.

Cobaltous-Cobaltic Oxide, Co_3O_4, is a compound corresponding to the magnetic oxide of iron, and is obtained when either of the other oxides of cobalt or the nitrate is heated in the air. It forms a black powder.

Cobaltic Oxide, Co_2O_3, corresponding to ferric oxide, is obtained as a dark-brown powder by gently igniting the nitrate.

Cobaltic Hydrate, $Co_2(OH)_6$, is obtained as a brownish-black precipitate if an alkaline hypochlorite is added to a cobaltous solution. This is dissolved by sulphuric acid with liberation of oxygen, and by warm hydrochloric acid with liberation of chlorine; cold dilute hydrochloric acid, however, dissolves it with scarcely any evolution of gas, forming Co_2Cl_6, which decomposes on heating, however, into cobaltous chloride and chlorine.

Cobaltous Sulphate, $CoSO_4.7H_2O$, forms dark-red, monoclinic prisms.

Cobaltous Nitrate, $Co(NO_3)_2.6H_2O$, forms red, deliquescent prisms.

Cobalt Silicates.—When glass of any variety is fused with a cobalt salt a dark-blue color is obtained. This colored glass, when reduced to a powder, is used as a pigment under the name of *smalt*. The application of ores of cobalt for this purpose appears to date from the sixteenth century. Commercial smalt, made from sand, potashes, and roasted cobalt ores, contains usually from 6 to 16 per cent. of cobalt.

Two other pigments are also obtained from cobalt oxide: *Thenard's blue* (or cobalt ultramarine), by igniting it with alumina, and *Rinman's green*, by igniting it with zinc oxide.

of osmium, iridium, ruthenium, and rhodium, known as *osmiridium.* The platinum is thrown down from the solution by ammonium chloride as the double chloride of platinum and ammonium. This, when ignited, leaves the metal in a finely-divided state known as *spongy platinum.* The last substance is compressed into a cake by powerful pressure, and is then welded at a white heat into a homogeneous mass. Deville's method, however, has almost entirely superseded that just mentioned. In this the platinum ore is melted with an equal weight of galena and half its weight of metallic lead. The platinum is thus taken up by the lead while the osmiridium remains unattacked. The platinum-lead alloy is then melted and exposed to a current of air, by which the lead is oxidized, the oxide flowing off as slag and the platinum being left as a porous mass. This is placed in a furnace made of lime, and melted by means of a powerful oxyhydrogen blow-pipe flame.

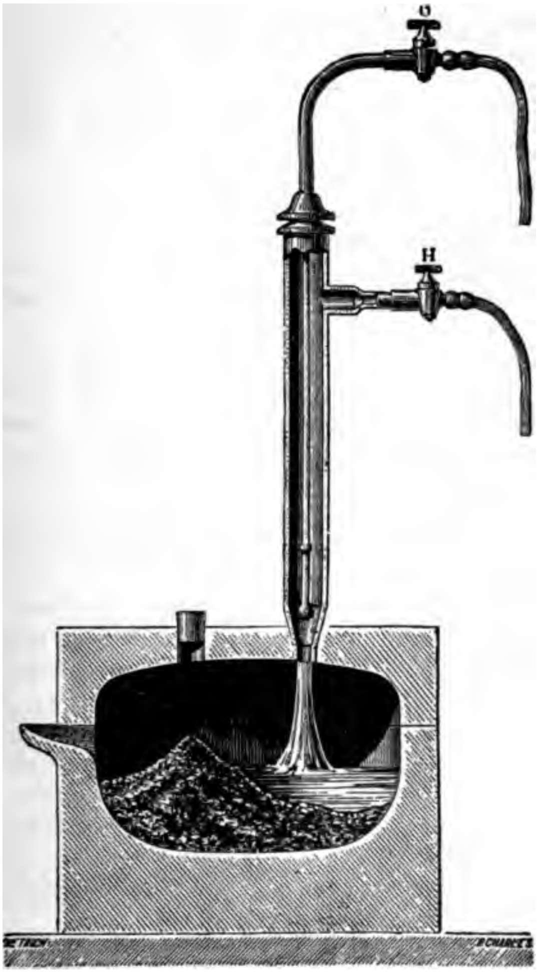
The accompanying figure shows the apparatus used for this purpose. The nozzle of the oxyhydrogen blast-lamp is introduced through a perforation in the dome of the furnace, through which, also, another opening is made for the introduction of the porous metal. From the lip-shaped exit at the side the melted metal may be poured into moulds.

Properties.—In the compact state platinum is of white color. It possesses a decided metallic lustre, great malleability, susceptibility of polish, and solidity. Next to gold and silver it is the most ductile of metals. Its malleability is considerably lessened by contamination with other metals, and is particularly noticeable in commercial platinum which contains iridium. Platinum belongs to the most difficultly fusible metals. Except in a very attenuated state and in small quantity, it requires the heat of the oxyhydrogen flame or the flame from the combustion of coal-gas in oxygen to melt it. Deville placed its melting point at 2000°. Like iron it can be welded at a white-heat. It crystallizes in cubes and octohedra. The specific gravity of the melted metal is 21.15, of the hammered metal 21.45. At no temperature does it combine with oxygen. Like copper and silver, the melted metal possesses the property of absorbing oxygen, which, as the metal is allowed to cool, is given off, causing the phenomenon of "spitting."

Compact platinum does not absorb oxygen, but it condenses this gas on its surface, and partly changes it to ozone. This occurs even at 50°.

trongly oxidizing action of the metal in such a condition conveniently illustrated by heating a small piece of platil in the flame of a Bunsen burner, and then quickly ex-

Fig. 90.



Platinum furnace.

ing the flame, allowing the gas to escape. The foil glows, laced near the burner it becomes hot enough to inflame . That this property is due to surface action seems to be by the fact that the more finely-divided forms of the metal, *platinum-black* and *spongy platinum*, possess the same properties to still higher degrees.

Platinum absorbs hydrogen at a red heat and holds it at ordinary temperatures, but at a red heat *in vacuo* the gas is given off. When platinum is employed as the negative pole in the electrolysis of water, it takes up hydrogen, which it will again give up by the employment of the hydrogen-laden metal as positive pole.

When platinum is reduced from its chlorine compounds it is obtained in an extremely finely-divided condition, and is then known as *platinum-black*.

This reduction may be brought about by the action of metallic zinc, or by boiling the solution with an alkali hydrate or carbonate and adding some organic substance, such as sugar or alcohol. In the form of platinum-black, the metal is capable of condensing several hundred times its volume of oxygen. It thus becomes an energetic oxidizing agent; alcohol thrown upon it is at once ignited. Some authorities regard platinum-black as an oxide. It is a black, hard powder, which, by great pressure and rubbing, may be made to assume a white color. Repeated heating reduces its power to condense oxygen.

Under no circumstances does platinum decompose water. Hydrochloric, hydrofluoric, nitric, and pure sulphuric acids singly do not attack platinum.

Nitro-hydrochloric acid easily and completely dissolves it.

When alloyed with silver it is dissolved by nitric acid.

Fused alkali sulphides, hydrates, cyanides, and nitrates all attack the metal. It is also affected by the free elements or by mixtures which liberate the halogens. Platinum-ware should never be heated in the inner cone of a Bunsen-burner flame, as it is likely to combine with the carbon of the gas to form a compound which injures the texture of the metal. Platinum vessels are usually cleaned by rubbing with moistened round sea-sand, or by fusing in them a quantity of acid potassium sulphate until white fumes of sulphur trioxide are evolved.

Platinum-sponge finds use in Döbereiner's tinder-box, in which nascent hydrogen is inflamed by passing over the porous metal.

Platinum is made into stills for use in distilling sulphuric acid.

The metal was at one time used in Russia for the coinage of money.

The production of platinum in Russia for the year 1891 was 4226 kilos.

When iridium is present in platinum it does not disqualify it for the preparation of apparatus, but, on the contrary, better adapts it for such purposes, inasmuch as it makes the articles less fusible, more rigid, harder, denser, and less readily attacked chemically than pure platinum. An alloy of 8 parts of platinum and 2 parts of iridium is only very slightly dissolved by nitro-hydrochloric acid. An alloy containing 10 per cent. of iridium was used in France to prepare the standard metre and kilogramme.

Porcelain is ornamented with platinum by applying a thin paste made from platinum and ammonium chloride by the aid of rosemary and lavender oils, the article being subsequently heated in a muffle. To coat metallic objects, a paste of the same salt but with tartaric acid, or the metal in the form of a very thin foil, is strongly rubbed on, or the article may be suspended in a regular plating bath of the double chloride dissolved in a solution of sodium carbonate.

PLATINUM AND THE HALOGENS.

Platinous Chloride, $PtCl_2$, is obtained by heating spongy platinum in a stream of dry chlorine to 240°–250°.

It is a gray-green powder, insoluble in water, but soluble in hot hydrochloric acid to give a red-brown colored solution.

Chloroplatinic Acid, $PtCl_4,2HCl.6H_2O$, results when platinum is dissolved in nitro-hydrochloric acid and the solution evaporated with hydrochloric acid to expel nitric acid. By completing the evaporation over sulphuric acid or caustic lime a deliquescent salt is obtained.

It is used in platinum-plating and as a reagent for potassium.

Platinic Chloride, $PtCl_4.5H_2O$.—When a molecule of chloroplatinic acid is decomposed with two molecules of silver nitrate and the resulting precipitate filtered off, a yellowish-red, silver-free solution is obtained, which, upon evaporation, yields platinic chloride as a red, crystalline, non-deliquescent salt.

Both chloroplatinic acid and platinic chloride form with the chlorides of potassium and ammonium difficultly-soluble, yellow, crystalline, double chlorides. The corresponding sodium and lithium compounds are soluble.

Platinous Bromide, $PtBr_2$, results as a brown-gray, insoluble mass when bromoplatinic acid is heated to 200°.

Platinic Bromide, $PtBr_4$, is not known except in combination with hydrobromic acid as bromoplatinic acid. The latter is produced by dissolving platinum in a mixture of nitric and hydrobromic acids; it crystallizes in deliquescent, dark-red prisms.

Platinous Iodide, PtI_2, is a black powder obtained by warming platinous chloride with potassium iodide.

Platinic Iodide, PtI_4.—By heating an excess of chloroplatinic acid with potassium iodide a black powder, insoluble in water and soluble in potassium iodide, is obtained.

PLATINUM AND OXYGEN.

Platinous Oxide, PtO, and *Platinic Oxide*, PtO_2, are obtained as black powders by careful heating of the respective hydrates.

Platinous Hydrate, $Pt(OH)_2$, forms a black powder which possesses the characters of a weak base. It is obtained by digesting platinous chloride with potassium hydrate.

Platinic Hydrate, $Pt(OH)_4$, is obtained as a white, flocculent precipitate by boiling chloroplatinic acid with an excess of sodium hydrate, and then acidifying the liquid with acetic acid.

Platinous Sulphide, PtS, and *Platinic Sulphide*, PtS_2, are precipitated from the corresponding chlorides when the latter, in water solution, are treated with hydrogen sulphide. They are black-brown powders.

Platinum forms many series of ammonium compounds. Fulminating platinum is produced by decomposing platinum and ammonium chloride with potassium hydrate. It is a straw-colored powder whose composition has not been determined.

RHODIUM.

Symbol, Rh. *Atomic Weight*, 102.9. *Valence*, II and IV.

Wollaston discovered this element in an American platinum ore in 1804, and on account of the rose-red color of its chloride gave to it the name rhodium. Apart from its occurrence in platinum ores, rhodium occurs alloyed with gold. In the compact state it is a gray-white, malleable metal, which is more difficultly fusible than platinum, but more easily than iridium. Its specific gravity is 12.1. It oxidizes superficially, becoming blue when strongly heated in the air or in contact with alkalies. Rhodium is insoluble in all acids with the exception of nitro-hydrochloric. Its alloys are, however, more easily dissolved. At a red heat chlorine produces with the finely-divided metal red, insoluble rhodium chloride, Rh_2Cl_6.

Rhodium gives oxides of the following compositions: RhO, Rh_2O_3, and RhO_2. The hydrates, $Rh(OH)_4$ and $Rh_2(OH)_6$, are known.

The oxygen salts of rhodium, as also the other compounds, have as yet found no practical application.

RUTHENIUM.

Symbol, Ru. *Atomic Weight*, 101.4. *Valence*, II and IV.

Ruthenium was first observed in 1828, by Osann, in the residues from the working of the Russian platinum ores.

The name ruthenium was applied to the new element because the ores came from Russia. It was first prepared in a pure state by Claus, in 1848.

It also occurs as sulphide in *laurite*, which is found along with platinum ores in Borneo and Oregon.

Ruthenium is a gray-white, brittle metal, which, with the exception of osmium, is the most difficultly fusible of the members of the platinum group.

When melted the metal is somewhat oxidized. The specific gravity of uthenium is 12.26. The acids, including nitro-hydrochloric acid, fail to dissolve it.

At a low red heat the metal combines with chlorine to give ruthenium dichloride, $RuCl_2$. The other chlorides known are Ru_2Cl_6 and $RuCl_4$.

Besides oxides and hydrates of the same constitution as those yielded by rhodium, ruthenium also forms RuO_2 and RuO_4. By fusing the finely-divided metal with potassium hydrate and potassium nitrate, potassium utheniate, K_2RuO_4, is obtained. It dissolves in water with a red-yellow color; the solution blackens the skin. Nitric acid throws down from the water solution a black precipitate of ruthenium sesquihydrate, $Ru_2(OH)_6$, which dissolves in hydrochloric acid with an orange-red color.

A brown sulphide is known.

These compounds are only of scientific interest.

PALLADIUM.

Symbol, Pd. *Atomic Weight*, 106.35. *Valence*, II and IV.

In 1803 palladium was discovered by Wollaston in native platinum. He named it after the then recently discovered planet Pallas. It is alloyed with platinum in almost all ores in which the last metal is found. To some extent it occurs in the pure state, in the form of small, flattened grains, which are mixed with the Brazilian platinum ores.

A Brazilian gold ore which contains from 5 to 10 per cent. of palladium forms its chief source. In its appearance, lustre, hardness, and malleability this metal is very similar to platinum. It is the most fusible of the platinum metals. Heated in air it becomes superficially oxidized, but at a higher temperature regains its lustre.

It has a specific gravity of 11.4.

Hot, strong mineral acids and alkalies attack the metal. This element has an affinity for hydrogen that has characterized it above all others. Palladium hydride, Pd_2H, which contains about 600 volumes of hydrogen, is the product of the union, and is considered to be an alloy of the elements whose formation takes place most favorably at 100°. In forming this compound the metal is said to *occlude* the gas. Palladium generally occurs in commerce in foil. It is used to some extent for the mountings of physical and mathematical instruments and in dental wares.

Of the chlorine compounds of the metal only palladious chloride, $PdCl_2$, is known in the isolated state, although palladic chloride, $PdCl_4$, may result when the metal is dissolved in nitro-hydrochloric acid. When this solution is evaporated chlorine is given off, and brown-red prisms, having the composition $PdCl_2.2H_2O$, are obtained. The aqueous solution of the last salt serves for the quantitative separation of iodine from bromine and chlorine.

Palladious Oxide, PdO, and *Palladic Oxide*, PdO_2, are black powders, difficultly soluble in acids. *Palladious Hydrate*, $Pd(OH)_4$, and *Palladic Hydrate*, $Pd(OH)_4$, are only little known. The metal acts bivalent in all its stable oxygen salts.

IRIDIUM.

Symbol, Ir. *Atomic Weight*, 192.5. *Valence*, II and IV.

Iridium was discovered along with osmium in 1804, by Smithson Tennant, in the *osmiridium* left in the working of platinum ores. On account of the manifold colors which the solution of its chloride showed, he designated it by its present name. Besides the above source it is sometimes found alloyed with platinum alone. Iridium forms in the compact state a pure white, steel-like, lustrous, brittle metal. It is harder and less fusible than platinum, and has a specific gravity of 22.4. It behaves somewhat like palladium when heated in air or oxygen. In the compact state it is insoluble in all acids. Only in the divided state is it soluble in nitro-hydrochloric acid to give iridium tetrachloride, $IrCl_4$.

Fusing alkali hydrates convert the metal into sesquioxide.

Chlorine at a low red heat gives a chloride of the formula Ir_2Cl_6, but in the presence of sodium chloride, however, iridium tetrachloride, $IrCl_4$. From the solutions of its salts, zinc and iron separate black metal.

The oxides and hydrates of iridium have the following formulas: IrO, Ir_2O_3, IrO_2, $Ir(OH)_2$, $Ir_2(OH)_6$, and $Ir(OH)_4$. They are all recognized as compounds having weak properties both as acids and bases. Their salts are but little known. Platinum is alloyed with iridium to increase its resistance to chemicals. It is used to tip gold pens, which are thereby rendered much more durable. To impart a black color, both the finely-divided metal and the sesquioxide are used in porcelain decorations.

OSMIUM.

Symbol, Os. *Atomic Weight*, 190.3. *Valence*, II and IV.

Osmium was discovered in 1804, by Smithson Tennant, along with iridium, in the *osmiridium* or insoluble residue left upon treatment of the platinum ores with nitro-hydrochloric acid.

The name is from the Greek word ὀσμή, meaning odor.

The metal, when finely powdered, emits a peculiar, pungent, iodine-like odor, in consequence of the formation of osmic anhydride, OsO_4. Osmium is the heaviest metal known, having the specific gravity of 22.47. It is hard, bluish-white, and volatile at the temperature of melting iridium It has never been melted. The metal combines with chlorine to give *osmium dichloride*, $OsCl_2$, and *tetrachloride*, $OsCl_4$. *Osmium sesquichloride*, Os_2Cl_6, is not known in the free state.

The following oxides and hydrates are known: OsO, Os_2O_3, OsO_2, OsO_4, $Os_2(OH)_6$, and $Os(OH)_4$.

Fuming nitric acid and nitro-hydrochloric acid convert osmium into osmic anhydride, OsO_4, which is also produced by melting the metal with potassium nitrate. Osmic anhydride forms colorless, glistening needles, which volatilize without decomposition. The vapors emitted by this substance are irritating to the eyes and suffocating. It is soluble in water, giving a colorless, neutral solution, which has a caustic taste and the peculiar iodine-like odor of the anhydride.

Osmic anhydride is an oxidizing agent. It is used as a stain in histological work.

Osmic acid, H_2OsO_4, is not known in the free state.

When alcohol is added to a solution of the anhydride in potassium hydrate a reddish precipitate of potassium osmate, $K_2OsO_4.2H_2O$, is thrown down.

The great hardness of osmiridium is taken advantage of for cutting glass, as also for the manufacture of the points of writing pens.

Owing to the peculiar tendency of the carbon atoms to
gate together in groups and the facility with which the satu
hydrogen of "hydrocarbons," as the combinations of thes
elements are called, is replaced, the number of carbon comp
capable of formation is an immense one. Besides the
thousands of these carbon compounds naturally occurrin
number artificially formed has grown enormously in recent
It becomes eminently desirable, therefore, to classify then
study them apart from the compounds of the other element

2. Composition and Analysis of Organic Compou
—Many organic compounds contain carbon and hydrogen
and are known as "hydrocarbons." The other elements
at times as constituents of organic compounds are oxyge
nitrogen, and less frequently sulphur and phosphorus.
halogens and other elements are often introduced by substit
into the formulas of organic bodies.

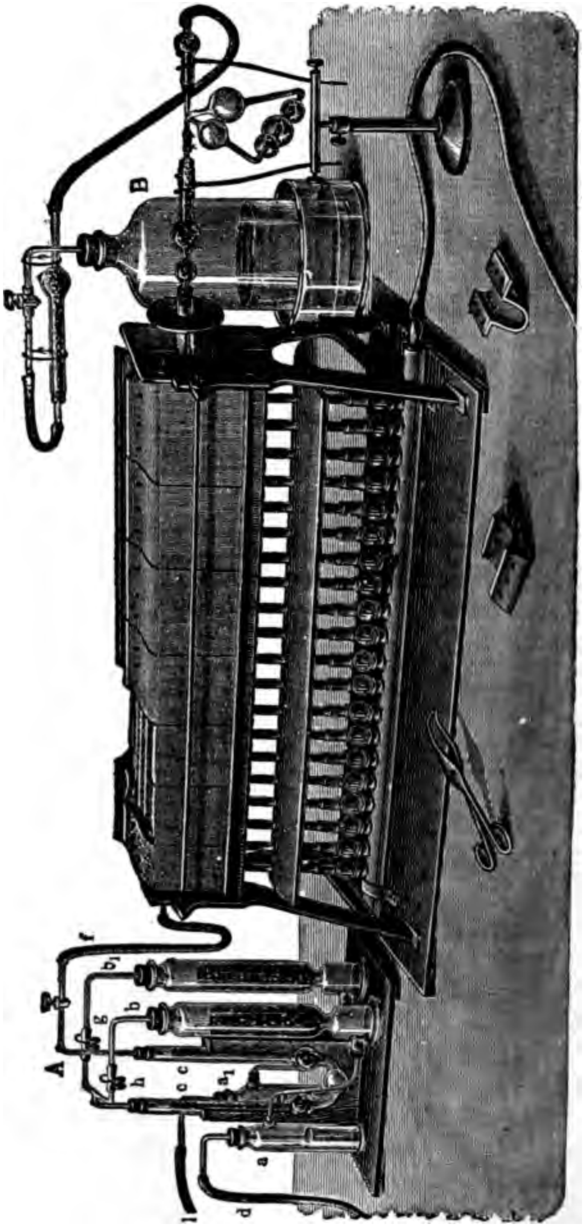
The analysis of the carbon compounds may be either *qu*
tive or *quantitative*, and both of these methods may be ap
with reference to the *ultimate* (or *elementary*) and the *prox*
composition of the substance analyzed.

(*a*) *Qualitatively*, carbon is shown in many cases by
charring which takes place when the substance is heated
strip of platinum foil. In case the material is volatile wi
decomposition, it is mixed with easily reducible substances,
as copper oxide or chromate of lead, placed in a tube seal
one end, and heated, when the carbon is oxidized to ca
dioxide. The escaping gas may be conducted through
water, and the presence of carbon will be indicated by the
bidity produced in this.

The same mixture of the suspected organic compound
oxide of copper or chromate of lead when heated will give
to the formation of water if hydrogen is present. This will
dense in the cooler part of the tube or may be received in a
containing calcium chloride.

The nitrogen in many organic compounds is indicated by
decomposition on heating with evolution of the odor of b
feathers. Such substances heated in a tube closed at one
with soda-lime (a mixture of caustic soda with lime) will giv
ammonia, readily recognizable by its odor or by the use of
litmus paper. Some nitrogenous compounds do not respon
this test. A test applicable, however, to all organic nitroge
compounds is to heat the substance in a small dry test-tube

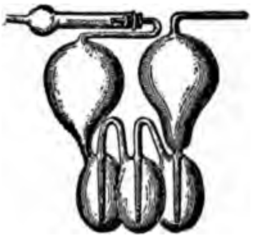
FIG. 91.



Gas combustion furnace.

:he end ,of the heating it may be broken and a current of ified air or oxygen passed through, or a tube open at both s is taken. In the latter case the combustion is carried out n beginning to end in a current of purified oxygen. The ification of the oxygen or of a current of air is effected in the aratus shown in the cut as connected with the rear end of the ıbustion tube. Oxygen entering through the tube *d* passes ›ugh sulphuric acid in *a*, a chloride of calcium jar at *b*, and tube filled with stick potash at *c c*, and then through the *f* to the combustion tube. A second series of absorption sels on the same stand serves for air. The water produced the oxidation of the hydrogen of the organic substance is ght in a weighed tube containing fused and granulated chlo- : of calcium, and the carbon dioxide produced by the oxi- .on of the carbon of the organic substance is caught in a ghed bulb apparatus containing strong caustic potash solu- ι. Instead of the older form of potash bulbs known as the big bulbs shown in Fig. 91, the apparatus of Geissler shown 'ig. 92 is now more generally used because of the convenience veighing. One-ninth of the increase reight of the chloride of calcium tube resents the weight of the hydrogen, le three-elevenths of the increase of ght of the potash bulbs represents weight of the carbon.

FIG. 92.



Geissler's potash bulbs.

f the organic compound is nitro- ıous, a spiral of metallic copper or rer must be placed in the front end the combustion tube and kept at a r red heat in order to prevent the ides of nitrogen from going over in the absorption apparatus d vitiating the results. Organic compounds containing sul- ur must be burned with chromate of lead, which will oxidize e sulphur and hold it as sulphate of lead. Halogens present an organic compound are held as silver haloid salts by the use the silver spiral before alluded to.

The nitrogen of an organic compound is either determined ›solutely and its volume measured, or it is converted into am- onia by combustion with soda-lime as in the Will-Varrentrap ethod, or by heating with strong sulphuric acid and potassium :rmanganate as in the Kjeldahl method. In the determination f nitrogen by volume a tube closed at one end is used, and in the farther end sodium bicarbonate or magnesite is placed. This is first heated so as to displace all the air of the tube by carbon dioxide, and then the substance is burned with copper oxide, a copper spiral being used of course in the front end of the tube to decompose oxides of nitrogen. The nitrogen gas is collected over strong potash solution, which absorbs the carbon dioxide and allows of the measurement of the volume of residual nitrogen. In the soda-lime process the substance is burned in a tube closed at one end, somewhat shorter than the ordinary combustion tube, and the ammonia produced is absorbed in pure strong hydrochloric acid. We may then either determine the ammonia here caught as sal ammoniac by the use of platinic chloride, or, if a measured amount of hydrochloric acid of known strength was taken, may titrate back with normal alkali solution and so determine the ammonia indirectly. In the Kjeldahl process the substance is heated with concentrated sulphuric acid for some time to a temperature near the boiling point of the latter, the addition of small portions of powdered potassium permanganate near the end of the action sufficing to complete the ammonia formation. The mixture is then diluted with water, supersaturated with caustic soda, and the ammonia distilled off and determined volumetrically.

The methods for the determination of the halogens, sulphur and phosphorus have already been indicated in speaking of their qualitative detection.

Oxygen is always determined by difference, as no reliable general method for its determination exists.

3. Physical Properties of Organic Compounds.—The physical properties are just as important points for observation in the case of organic compounds as with inorganic substances, only, instead of crystalline form, hardness, lustre, color, etc., the important properties for consideration in this connection are fusing point, boiling point, vapor-density, and in some cases optical properties.

(*a*) *Fusing Point.*—Most organic solids, when sufficiently pure fuse either with or without decomposition at a constant temperature. To determine the fusing point, a small quantity of the substance carefully dried and pulverized is placed in a capillary tube sealed at one end, and this is attached by a rubber band to a thermometer in such a way that the capillary tube with the substance is immediately adjacent to the bulb of the thermometer. A round-bottomed flask with a long neck is then taken, and in this is placed concentrated sulphuric acid or paraffin so that the few fixed temperatures corresponding to the boiling points of the components of the original mixture.

The process of fractional distillation is much facilitated by the use of distillation bulbs with special arrangements for condensation in the vertical neck attached to the bulb or flask, such as the apparatus of Wurtz, Linnemann, and Hempel. These accomplish a fractional condensation of the vapors corresponding to that effected in the column apparatus of the rectifier or tar distiller.

(*c*) *Vapor-density.*—We have already explained the relationship between vapor-density and molecular weight and the principles upon which it is based (see page 121). This determination has considerable importance in the study of organic compounds, as, for reasons to be explained later, ultimate organic analysis does not generally enable us definitely to determine molecular weight and molecular formulas. Hence a physical determination which can go so far towards settling the question of chemical composition becomes very important.

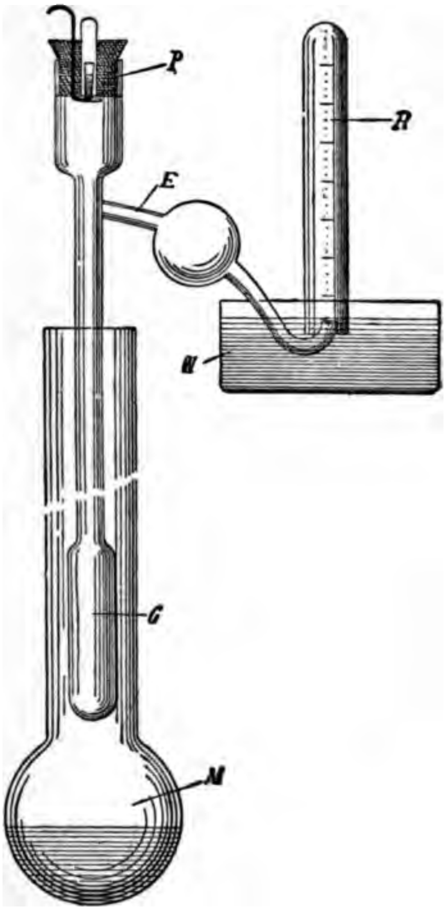
For determination of vapor-density we can ascertain the weight of a definite volume of the vapor, which is then compared with the weight of the same volume of air under similar conditions of temperature and pressure, or the volume occupied by the vapor obtained from a fixed weight of the substance, or thirdly, the volume of another substance like mercury or air displaced by the vapor from a definite weight of the compound under investigation.

To the first class of determinations belongs the Dumas vapor-density method, in which globes of heavy glass with narrowed neck are used. These are weighed full of the vapor after the neck has been sealed by fusion of the capillary portion, and then opened under mercury so that the cubic contents of the globe can be accurately determined by measuring the mercury which fills it. The method is now rarely used.

To the second class of determinations belongs the Hofmann vapor-density method. In this case we have a tall barometer tube filled with mercury and dipping into a mercury trough. This is surrounded by a wider mantle-tube through which the vapor of water, aniline, or other higher-boiling liquid may circulate. Before the vapor is made to pass through the mantle, the weighed portion of the substance whose vapor-density is required is passed up into the barometer tube. Here, as the tube becomes heated by the vapor surrounding it, the substance vaporizes in vacuo. When the level of the mercury becomes constant in the tube, it is read off and the volume of vapor is calculated.

To the third class of determinations belongs the method of Victor Meyer, which is at the present time in most general use. The apparatus for this is shown in Fig. 93. The vessel in which the substance is to be vaporized is shown at G. This is closed by a cork perforated and fitted with a glass tube in which the little vessel with substance is placed as shown at P. The liquid in the mantle at M is first brought to boiling, and when air ceases to issue through the delivery tube at E, the eudiometer tube R is placed in position over the end of the delivery tube as shown in the illustration. The little tube containing the substance is then caused to fall by bending the wire support to one side. The vapor of the organic compound displaces an amount of air corresponding to its volume at the temperature of the experiment. Not more than 0.1 gramme of the substance is needed for this method. From the results of this determination, the vapor-density is calculated by the use of the following formula: $D = \frac{S.760(1.003665t)}{V.(B-w)0.001293}$, in which D stands for density, S for weight of substance, t for temperature, V for volume of air displaced, B for barometric reading, and w for tension of the vapor of water at the temperature of the obser-

FIG. 93.



Victor Meyer's vapor-density apparatus.

vation. Inasmuch as air is 14.435 times heavier than hydr the value D must be multiplied by 14.435 to obtain vapor-d based on hydrogen, and by 28.87 to get the molecular weig the substance used.

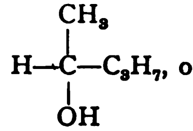
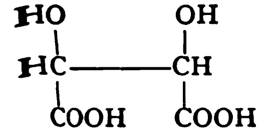
(*d*) *Optical Properties.*—Many organic compounds tur plane of polarization of light. This may happen with the in the solid state, as with benzile, $C_{14}H_{10}O_2$, or with others solid as well as when in solution, as with strychnine sulp but most generally it is shown in liquids only, as tartaric aci the sugars. Some liquids, like oil of turpentine, also show their vapors.

In many cases several optically active modifications same compound exist. Thus, a dextro-rotatory and a lævo tory modification can be obtained, as in the case of tartaric These will combine to form an inactive variety of the same pound. Conversely, the inactive variety can often be brok into the two optically opposed varieties. This may be do several ways. Inactive tartaric (racemic) acid may be transfo into the ordinary active variety by heating to 170° C., or th of the inactive acid will crystallize out as a mixture of th opposing varieties. The addition of certain ferments wil cause a change of an inactive variety into an active one.

The angle of rotation of the plane of polarized light case of an optically active substance is proportional to the ness of the layer traversed. It is also dependent upon the length of the light used for illumination in the instrument. low monochromatic light from a sodium flame is generally It is also somewhat dependent upon temperature.

When the specific rotatory power of a substance is know can, in the case of a solution containing this substance a only optically active ingredient, determine the percenta material present from an observation of the angle of actual tion. Thus, in the case of a sample of diabetic urine, we observed an actual rotation of +1.5°. Knowing the sp rotatory power of grape sugar to be 52.5° we make the calcul $p = \frac{100 \times 1.5}{52.5 \times 1} = 2.8$ per cent. grape sugar. In cas specific gravity of the solution is much over 1, that must be used, multiplying it into the denominator. The practic of the polariscope will be referred to again under *Sugars*.

An explanation of the optical activity of organic compo has been offered in recent years by Lè Bel and Van t'Hoff.

is that optically active compounds contain one or more *asymmetric* carbon atoms, that is, carbon atoms each of the four affinities of which are joined to a different atom or group, as in the case of optically active amyl alcohol,  $H-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}-C_3H_7$, or tartaric acid,  $\begin{array}{ccc} HO & & OH \\ | & & | \\ HC & — & CH \\ | & & | \\ COOH & & COOH \end{array}$. It has been found that all optically active substances contain such asymmetric carbon atoms, but the converse is not invariably true.

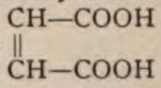
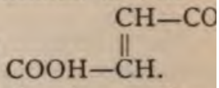
4. **Isomerism and Structural Formulas.**—The results of an ultimate combustion analysis of an organic compound will give us nothing more than the ratio of the atoms composing it. Even with the molecular weight obtained by means of a vapor-density determination, we can give only what is called an *empirical* formula; that is, one which expresses the number of the several atoms present but with no information as to how they are joined together. We find, however, that there are numerous cases where several bodies may exist having the same percentage composition, or even the same absolute number of the constituent atoms, and yet be quite different in physical properties. Thus, CH_2O, formaldehyde, $C_2H_4O_2$, acetic acid, and $C_3H_6O_3$, lactic acid, will have the same percentage composition although of different formulas. Again, pyrocatechin, resorcin, and hydroquinone all have the formula $C_6H_6O_2$ and yet are quite distinct in fusing points as well as in chemical reactions.

Bodies which have such points of agreement and yet are different are said to be *isomeric*.

We may distinguish four distinct cases of *isomerism*.

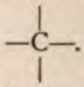
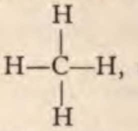
(*a*) When the isomeric bodies have the same percentage composition but a different molecular weight. Such bodies are said to be *polymeric*. Thus, C_2H_4, ethylene; C_3H_6, propylene; C_4H_8, butylene; C_5H_{10}, amylene, are polymeric, the unit of increment being CH_2. CH_2O, formaldehyde; $C_2H_4O_2$, acetic acid; $C_3H_6O_3$, lactic acid; $C_6H_{12}O_6$, grape sugar, are also polymeric.

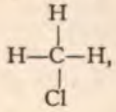
(*b*) When the isomeric bodies have the same molecular weight also. Such bodies are said to be *metameric*, as their difference is based upon a different arrangement of the atoms within molecule. Thus, trimethylamine and propylamine have eq the formula C_3H_9N ; methyl ether and ethyl alcohol have equ the formula C_2H_6O ; dextrose and levulose have equally the mula $C_6H_{12}O_6$.

(*c*) A third case of isomerism is what is termed *physical iso ism.* This is believed to be due to a different geometrical tion of the atoms in the molecule, as explained in the new ste chemical theories. Thus, fumaric and maleic acids are consid to differ from each other by the stereo-chemical distinction pressed in the formulas  $\begin{array}{l}CH-COOH\\ \|\\ CH-COOH\end{array}$ and  $\begin{array}{r}CH-CO\\ \|\\ COOH-CH.\end{array}$

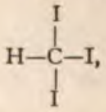
(*d*) We have yet the case of isomerism based upon chang the method of linking the hydrogen in the molecule. bodies are called *tautomeric.* Thus, the formula of hydr cyanide may be N≡C—H or C≡N—H, and two series of de tives readily changing into each other are formed, the cya and the isocyanides, according as one or the other mole grouping exists.

Formulas which show the method of the linking of the stituent atoms are called *rational* or *structural* formulas. importance in organic chemistry, where differences in compo may depend, as shown above, on the variations in the metho linking the elements, is obvious.

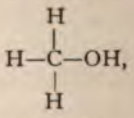
The tetrad character of the carbon element, to start wi represented thus :  $\begin{array}{c}|\\ -C-\\ |\end{array}$. When these four bonds of the ca are satisfied with hydrogen we have the fundamental h carbon  $\begin{array}{c}H\\ |\\ H-C-H\\ |\\ H\end{array}$, methane. The hydrogen atoms are re replaceable by monad atoms and groups, and the substit compounds so formed will be represented thus :



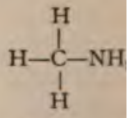
$\begin{array}{c}H\\ |\\ H-C-H,\\ |\\ Cl\end{array}$



$\begin{array}{c}I\\ |\\ H-C-I,\\ |\\ I\end{array}$

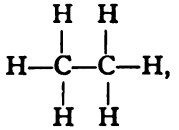


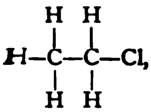
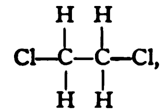
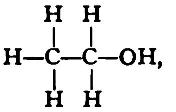
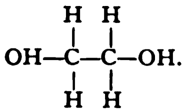
$\begin{array}{c}H\\ |\\ H-C-OH,\\ |\\ H\end{array}$



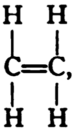
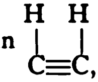
$\begin{array}{c}H\\ |\\ H-C-NH\\ |\\ H\end{array}$

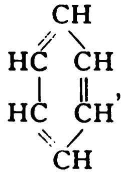
Several carbon atoms may be joined together by the ai one or more bonds furnished by each of the carbon atoms.

we have the hydrocarbon  $\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H}$, ethane. In this case and in all its substitution derivatives the use of the structural formula becomes of great assistance in showing the nature and relationship of the molecule. We have among these derivatives

 $\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}Cl}$,  $\mathrm{Cl{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}Cl}$,  $\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}OH}$,  $\mathrm{OH{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}OH}$.

A more condensed form of rational formula is sometimes employed, as $CH_3.CH_2Cl$, $CH_2Cl.CH_2Cl$, $CH_3.CH_2OH$, $CH_2OH.CH_2OH$, in which the saturation of each individual carbon atom is shown without the aid of the graphic formulas showing the bonds.

In  $\mathrm{\overset{H}{\underset{H}{C}}{=}\overset{H}{\underset{H}{C}}}$, ethylene, we have indicated a double linking of the carbon atoms, and in  $\mathrm{\overset{H}{C}{\equiv}\overset{H}{C}}$, acetylene, a treble linking. The hydrogen atoms of these compounds are of course replaceable by monad atoms or groups, as in the case of hydrocarbons with the single linking.

Still more important becomes the structural formula in the case of the benzene derivatives or aromatic compounds. Here the fundamental hydrocarbon benzene is represented,  that is, six carbon atoms alternately singly and doubly united, so that each carbon atom sacrifices three bonds in the linking of the molecule and has one free for combination with hydrogen or its equivalent replacing group.

Such a method of linking is generally known as the "closed-chain" structure, in distinction from the "open-chain" structure before shown with ethane and similar hydrocarbons.

5. Radicals, Residues, and Atomic Groups.—The residue

remaining after taking away one or more atoms from an o
compound is often called a *radical.* The valence of this
or residue depends upon the number of hydrogen atoms
must be added to make a saturated compound of it.

The relative importance of these radicals in the study
ganic compounds is so great that at one time organic che
was defined as the "chemistry of compound radicals."

Thus, by the withdrawal of one hydrogen atom from t
urated hydrocarbon methane, CH_4, we obtain the monad
cal methyl, CH_3; by the withdrawal of two hydrogen ato
get the dyad radical methylene, CH_2; by the withdrawal of
hydrogen atoms we get the triad radical methenyl, CH. Sim
from ethane, C_2H_6, we get the monad radical ethyl, C_2H
from propane, C_3H_8, we get the monad radical propyl,
These radicals are then very conveniently written as units
rational formulas of organic compounds, as $CH_3.Cl$ and CH
known as methyl chloride and methyl alcohol respective
$C_2H_5.Br$ and $(C_2H_5)_2O$, known as ethyl bromide and ethyl
respectively.

Many of the inorganic groups or radicals are made use o
in the rational formulas of organic compounds, as (OH
droxyl, $(NO_2)^{I}$ the nitro-group, $(NO)^{I}$ the nitroso-group, (
the amido-group, $(NH)^{II}$ the imido-group, $(N)^{III}$ the nitril-g
(—N=N—)^{II} the azo-group, and $(HSO_3)^{I}$ the sulphonic g

Of the organic radicals, besides methyl, ethyl, propyl,
already mentioned, we have the aldehyde group (CO.H
carboxyl group $(COOH)^{I}$, the ketone group $(CO)^{II}$, and t
anogen group $(CN)^{I}$.

6. Homologous Series.—We have already shown the g
formulas of methane and ethane, CH_4 and C_2H_6. By conti
the linking of the carbon atoms in the manner there sho
obtain propane, C_3H_8, butane, C_4H_{10}, pentane, C_5H_{12}, and
siderable series of hydrocarbons. It will be noticed that th
cessive members of this series differ by the constant incr
CH_2. Such a series of compounds is called an *homologous*
Not only may we have an homologous series of hydroc
but the homology may extend to the various classes of
derivatives. Thus, we have the homologous series of chl
$CH_3.Cl$, C_2H_5Cl, C_3H_7Cl, C_4H_9Cl, $C_5H_{11}Cl$, and the ho
gous series of alcohols CH_3OH, C_2H_5OH, C_3H_7OH, C_4H
$C_5H_{11}OH$.

The explanation of this constant increment CH_2 is had

compounds. All of these hydrocarbons, however, both satur
and unsaturated, are open-chain hydrocarbons.

2. Halogen Derivatives of the Hydrocarbons.—If
tained from the saturated hydrocarbons they are substitu
derivatives exclusively ; if formed from unsaturated hydrocar
they may be addition compounds as well.

3. Nitro-Derivatives.—These contain the monad group N
replacing H of the hydrocarbon. They do not form so rea
with the methane series of hydrocarbons as with benzene an
homologues.

4. Alcohols.—These are hydrates of the hydrocarbon r
cals and play the part of weak bases. They may be m
tomic, diatomic, etc., according as one, two, or more hy
gen atoms are replaced by the corresponding number of
groups.

5. Ethers.—The oxides of the hydrocarbon radicals,
responding to the metallic oxides of inorganic chemistry,
termed simple ethers. Two different hydrocarbon radi
may be united by one oxygen atom and so constitute a "mi
ether."

6. Thio-Ethers and Sulphonic Compounds.—The firs
these classes includes the sulphides of hydrocarbon radicals,
second contains the sulphonic group HSO_3.

7. Aldehydes and Ketones.—These classes represent
direct oxidation products of the alcohols. If the alcohol
tain the group $CH_2.OH$, that is, belongs to the class of prin
alcohols, by oxidation it will yield an aldehyde ; if the alcohol
the other hand, contain the group CH.OH, that is, belong
the class of secondary alcohols, by oxidation it will yiel
ketone. In the first case, the group $CH_2.OH$ is changed
oxidation into CO.H, the characteristic aldehyde group ; in
second case, the group CH.OH is changed by oxidation into
the characteristic ketone group.

8. Acids.—When the oxidation of the alcohols or basic
drates is carried to completion, in the case of primary alco
(those containing the $CH_2.OH$ group) the aldehyde is char
into the corresponding acid, the characteristic group of whi
COOH. Acids are monobasic, dibasic, etc., according to
number of such groups they contain.

9. Esters.—These are salts containing an organic radica
base, which is combined with either an inorganic or an org
acid.

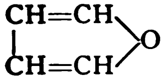
10. **Amines and Amides.**—Both these classes are ammonia derivatives. If the hydrogen atoms of the ammonia molecule are replaced by a basic radical we have an amine, if by an acid radical an amide.

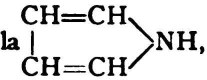
11. **Carbohydrates.**—These important compounds, known also as the "sugar and starch group," occupy the position of either aldehydes or ketones of hexatomic alcohols, and are treated as a separate group because of convenience and their common origin in the vegetable kingdom.

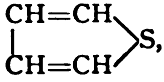
12. **Derivatives of Carbonyl.**—In these compounds the fundamental group is $(CO)^{II}$, which acts as an acid-forming radical.

13. **Derivatives of Cyanogen.**—In these compounds the fundamental group is $(CN)^{I}$, which acts in general like the halogen elements.

Intermediate between the open-chain hydrocarbons with their derivatives just enumerated and the closed-chain hydrocarbons of the benzene series (true aromatic compounds) are several groups.

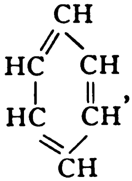
1. **Furfuran and its Derivatives.**—Furfuran, the starting-point of these compounds, has the structural formula  and shows a closed chain with four carbon atoms.

2. **Pyrrol and its Derivatives.**—Pyrrol, the underlying compound in this case, has the structural formula , and also shows a closed chain with four carbon atoms.

3. **Thiophen and its Derivatives.**—Thiophen, which is found as an accompaniment of benzene in coal-tar, has the structural formula , showing a closed chain with four carbon atoms.

The aromatic compounds, which, as said, form the second great class of organic substances, are derived from what are termed closed-chain series of hydrocarbons. Six atoms of carbon seem to join together in the closed-chain structure, and this molecule holds together through many reactions. We may also distinguish between aromatic compounds containing one nucleus and those containing more than one nucleus. Under the former class we have,—

1. **Hydrocarbons.**—These may be saturated, unsaturated, or addition hydrocarbons. They all contain the benzene nucleus,



, however, as the central feature of the molecule, and its hydrogen atoms may be replaced by hydrocarbon radicals, as $C_6H_5.CH_3$.

2. **Halogen Derivatives.**—The halogen derivatives of the benzene hydrocarbons may be of two kinds, either with the halogen replacing hydrogen of the nucleus, as $C_6H_4Cl.CH_3$, or hydrogen of the side-group, as $C_6H_5.CH_2Cl$. These two compounds are, it is seen, isomeric.

3. **Sulphonic Derivatives.**—These compounds contain the HSO_3 group replacing hydrogen. They are much more readily formed in the aromatic series than in the methane series and are correspondingly more important.

4. **Nitro-Derivatives.**—Here again the aromatic hydrocarbons are much more readily acted upon than the paraffin series. The action of strong nitric acid easily converts the hydrocarbons and many of their derivatives into the corresponding nitro-derivatives by replacing hydrogen by the group NO_2.

5. **Amido-Derivatives.**—By the action of reducing agents the nitro-derivatives are changed into the corresponding amido-derivatives, the NO_2 group being changed into the NH_2 group. These amido-derivatives, again, give rise to new compounds by the replacement of the hydrogen atoms of the NH_2 group by basic or acid radicals.

6. **Diazo- and Azo-Compounds. Hydrazines.**—Both the diazo- and the azo-compounds contain the dyad group —N=N—. In the former this group is combined on the one side only with a hydrocarbon radical, and in the latter on both sides with hydrocarbon radicals. The aromatic hydrazines are substitution derivatives of hydrazine, $NH_2—NH_2$.

7. **Phenols and their Derivatives. Quinones.**—The hydroxyl derivatives obtained by replacing by OH the hydrogen in the benzene nucleus of aromatic hydrocarbons are termed phenols. They act like weak acids. We may have monatomic, diatomic, and other phenols according to the number of OH groups so introduced.

The quinones are compounds in which two hydrogen atoms of the benzene nucleus are replaced by a dyad group (O_2).

8. Aromatic Alcohols, Aldehydes, and Ketones.—The aromatic alcohols are isomeric with the phenols, but contain the OH in the side-group, so that they contain the group CH_2OH, and hence are primary alcohols. The aromatic aldehydes are the products of oxidation of these alcohols.

The aromatic ketones, like the ketones of the methane series, contain the dyad group $(CO)^{II}$ linking together two hydrocarbon radicals, of which at least one contains the benzene nucleus.

9. Phenol Alcohols and Phenol Aldehydes.—When both hydrogen of the benzene nucleus and hydrogen of the side-group are replaced by OH groups, we have a phenol alcohol, and this by oxidation of the side-group yields a phenol aldehyde.

10. Aromatic Acids and Phenol Acids.—The product of the full oxidation of the aromatic alcohol is the aromatic acid. It contains the benzene nucleus joined with one or more COOH groups. If the benzene nucleus contain an OH group directly attached in addition, we have the phenol acid.

Under the head of aromatic compounds containing more than one nucleus we have several distinct cases to note.

1. Compounds with Several Uncondensed Nuclei.—We have here included the diphenyl group, the diphenyl-methane and triphenyl-methane groups, and the indigo group.

2. Compounds with Two Condensed Nuclei.—This includes naphthalene and its derivatives.

3. Compounds with Three Condensed Nuclei.—This includes anthracene, phenanthrene, and their derivatives.

4. Compounds containing Nitrogen in the Nucleus.—This includes pyridine, quinoline, and acridine, the first of which corresponds to benzene, the second to naphthalene, and the third to anthracene, with one CH group of the nucleus replaced by nitrogen.

The pharmaceutically and medicinally important classes of *alkaloids* and *ptomaines* follow next. While these compounds have not as yet been sufficiently studied to enable us to classify them in all respects, they appear to be in large part complex derivatives of the bases pyridine and quinoline just referred to.

The classes of *terpenes* and *camphors* are also important as present in the many naturally occurring *essential oils*. With these are also to be considered their products of oxidation, the *resins.* Of these several groups are noted, such as oleo-resins, gum-resins, balsams, and hard resins.

The important class of *glucosides* are also considered as supplementary to the regularly classified compounds because of the variety of their composition, as shown by the decomposition products. With them are also noted a number of technically important *dye woods* and other vegetable principles.

Lastly, the *protein substances* are to be considered. We note in this connection,—

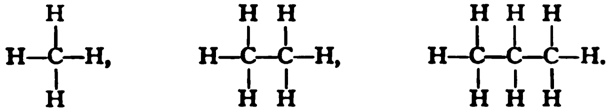
1. The classification of cell-forming substances.
2. The decomposition of proteid matter.
3. Ferments and enzymes.

CHAPTER II.

OPEN-CHAIN OR ALIPHATIC HYDROCARBONS.

I. THE SATURATED HYDROCARBONS, OR PARAFFIN SERIES.

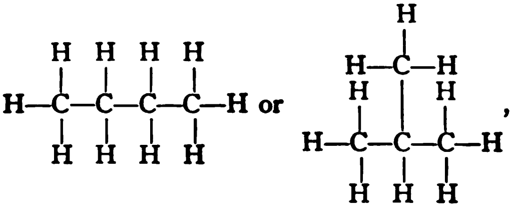
1. Composition, Nomenclature, and Molecular Constitution.—We have shown that, while the single atom of tetrad carbon can take up four atoms of hydrogen to form CH_4, two atoms of carbon, when linked together in the same molecule, can take up but six atoms of hydrogen, and three carbon atoms eight atoms of hydrogen. This is shown in the graphic formulas



$$\begin{array}{c}H\\|\\H-C-H,\\|\\H\end{array}\qquad\begin{array}{c}H\;\;H\\|\;\;\;|\\H-C-C-H,\\|\;\;\;|\\H\;\;H\end{array}\qquad\begin{array}{c}H\;\;H\;\;H\\|\;\;\;|\;\;\;|\\H-C-C-C-H.\\|\;\;\;|\;\;\;|\\H\;\;H\;\;H\end{array}$$

We have stated under the heading of "Homologous Series" that the difference between any two members of such a series is uniformly CH_2. We are, therefore, able to give a general formula for the entire series, by means of which the formula of any individual hydrocarbon in the series can be deduced. This general formula is C_nH_{2n+2}; that is, for a given number of carbon atoms there will be needed for saturation twice as many hydrogen atoms plus two. More than that number, it is seen from the graphic formulas, cannot be attached.

The first three hydrocarbons of this series, CH_4, C_2H_6, C_3H_8, can only be written structurally as represented above. The next one, however, C_4H_{10}, may be written in either one of two ways,—



$$\begin{array}{c}H\;\;H\;\;H\;\;H\\|\;\;\;|\;\;\;|\;\;\;|\\H-C-C-C-C-H\\|\;\;\;|\;\;\;|\;\;\;|\\H\;\;H\;\;H\;\;H\end{array}\text{ or }\begin{array}{c}H\\|\\H-C-H\\H\;\;\;|\;\;\;H\\|\;\;\;|\;\;\;|\\H-C-C-C-H\\|\;\;\;|\;\;\;|\\H\;\;H\;\;H\end{array}$$

, or more compactly

$$CH_3.CH_2.CH_2.CH_3 \text{ and } \left.\begin{matrix}CH_3\\CH_3\\CH_3\\H\end{matrix}\right\} C.$$

In fact, these different graphic formulas represent two distinct compounds, one boiling at +1° C. and the other at —17° C., and known respectively as normal butane and iso-butane, wh are isomeric with each other. In the case of C_5H_{12}, three i meric compounds are possible and have been prepared, and w C_6H_{14} five isomers are possible and are known.

The hydrocarbons of this series have been prepared as far $C_{35}H_{72}$. They are named by taking the names first applied the radicals in the case of the first four members of the series, after that the Greek numerals, and applying the uniform termi tion *ane*. A table of the hydrocarbons of the paraffin ser with melting and boiling points, is attached.

SATURATED HYDROCARBONS—C_nH_{2n+2}.

Formula.	Name.	Melting Point.	Boiling Poi
CH_4.	Methane	—186°	—164°
C_2H_6.	Ethane	. . .	gas.
C_3H_8.	Propane	. . .	—17°
C_4H_{10}.	Normal Butane	. . .	+1°
“	Iso-Butane	. . .	—17°
C_5H_{12}.	Normal Pentane	. . .	+37°
“	Iso-Pentane	. . .	+30°
“	Tertiary Pentane	— 20°	+9°
C_6H_{14}.	Hexane	. . .	69°
C_7H_{16}.	Heptane	. . .	98°
C_8H_{18}.	Octane	. . .	124°
C_9H_{20}.	Nonane	—51°	150°
$C_{10}H_{22}$.	Decane	—32°	173°
$C_{11}H_{24}$.	Undecane	—26°	195°
$C_{12}H_{26}$.	Dodecane	—12°	214°
$C_{13}H_{28}$.	Tridecane	—6°	234°
$C_{14}H_{30}$.	Tetradecane	+5°	253°
$C_{15}H_{32}$.	Pentadecane	10°	270°
$C_{16}H_{34}$.	Hexadecane	18°	287°
$C_{17}H_{36}$.	Heptadecane	22°	303°
$C_{18}H_{38}$.	Octadecane	28°	317°
$C_{19}H_{40}$.	Nonadecane	32°	330°
$C_{20}H_{42}$.	Eicosane	37°	205°
$C_{21}H_{44}$.	Heneicosane	40°	215°
$C_{22}H_{46}$.	Docosane	44°	224°
$C_{23}H_{48}$.	Tricosane	48°	234°
$C_{24}H_{50}$.	Tetracosane	51°	243°
$C_{27}H_{56}$.	Heptacosane	60°	270°
$C_{31}H_{64}$.	Hentriacontane	68°	302°
$C_{32}H_{66}$.	Dotriacontane	70°	310°
$C_{35}H_{72}$.	Pentatriacontane	75°	331°

2. Occurrence, Preparation, and Description of the M Important.—The hydrocarbons of the paraffin series occur ab dantly, ready formed in nature, in various crude petroleums. T lower members of the series, which are gaseous at ordinary temperatures, also occur as natural gas, which escapes from the earth in many localities; the middle members of the series make up the bulk of the petroleums, and hold dissolved, when first taken from the earth, both the gases and the higher members of the series, which are solids. These latter may occur by themselves also as ozokerite, or natural paraffine.

These hydrocarbons are also formed in the dry distillation of many naturally-occurring substances, such as bituminous coal, shales, wood, and from fish oils when distilled under strong pressure.

The first of the series, *methane*, is also found abundantly in nature as a product of decomposition, and owes its common name, "marsh gas," to such occurrence. Mixed with small quantities of carbon dioxide and nitrogen, it is formed whenever vegetable matter decomposes in the presence of water, as in the bottom of marshes and springs. Its formation here is due to the slow decomposition of the woody fibre under the special conditions of moisture, and probably the presence of micro-organisms, as it is known that cellulose may undergo a fermentative decomposition in their presence, with carbon dioxide and methane as sole products, according to the reaction: $C_6H_{10}O_5 + H_2O = 3CO_2 + 3CH_4$.

Methane also forms by the slow decomposition and change of bituminous coal, and hence is present in abundance in the galleries of coal-mines which are not properly ventilated. When mixed with air it constitutes the dangerous and explosive mixture known as "fire-damp." Under the name of "light carburetted hydrogen" it is known also in the distillation products of these coals. Thus, coal gas, as manufactured for illuminating purposes, contains from 30 to 40 per cent. of methane; "water gas," made by the action of steam on incandescent carbon, contains from 6 to 12 per cent.; while natural gas, now used in large quantities for fuel purposes, contains from 90 to 95 per cent. of methane.

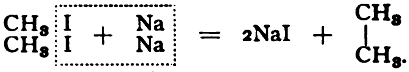
Methane may be artificially formed by a variety of methods:

Thus, carbon monoxide and hydrogen may be made to unite under the influence of electricity: $CO + 3H_2 = CH_4 + H_2O$.

Or a mixture of carbon disulphide vapor and hydrogen sulphide passed over ignited copper will react: $CS_2 + 2H_2S + 8Cu = CH_4 + 4Cu_2S$. It is generally formed (although somewhat contaminated with ethylene and hydrogen) by the heating of anhydrous sodium acetate and soda-lime, according to the reaction $CH_3COONa + HONa = CH_4 + CO\left\{\begin{matrix}ONa\\ONa\end{matrix}\right.$, methane and sodium carbonate being in theory the sole products. Chemically pure methane is obtained by the reduction of methyl iodide, CH_3I in alcoholic solution with copper-coated zinc (Gladstone and Tribe copper-zinc couple).

Methane is a colorless and odorless gas, condensable to a liquid under a pressure of 180 atmospheres at —11° C. It boils at —164° and solidifies at —186°. It burns with a pale, faintly lumiminous flame, and forms an explosive mixture with air.

Ethane is found in crude petroleum and in natural gas, and may be formed artificially by the action of zinc or sodium upon methyl iodide, as follows:



$$\begin{array}{l}CH_3\\CH_3\end{array}\boxed{\begin{array}{l}I\\I\end{array} + \begin{array}{l}Na\\Na\end{array}} = 2NaI + \begin{array}{c}CH_3\\|\\CH_3.\end{array}$$

It is a colorless and odorless gas, which can be liquefied at +4° by a pressure of 46 atmospheres. It burns with a pale flame.

Propane, normal *butane*, and normal *hexane*, all occur in crude petroleum, the latter two especially being present in gasoline and similar light fractions. Normal *heptane*, in addition to being present in petroleum, occurs in the oil from the *Pinus sabiniana*, or nut-pine, of California, and under the special name of "abietene" is used as a cleansing and solvent benzine.

The hydrocarbons from $C_{16}H_{34}$ on are solid at ordinary temperatures, and make up the bulk of the products known as *petrolatum*. A mixture of these hydrocarbons of still higher fusing point constitutes the commercial product known as *paraffine*.

The name paraffin (from *parum affinis*), first applied to the solid products as obtained from bituminous coals, has been applied to the whole series of hydrocarbons to indicate the stable character of these compounds. They are incapable of combining with halogens or taking up any additional hydrogen, are not affected by any of the strong acids in the cold, and only slightly when heated, and are not easily oxidized by chromic acid or potassium permanganate.

3. Pharmaceutically Important Products.—The first of these is **Benzinum,** U. S. P., and is stated to be "a purified distillate from American pretroleum consisting of hydrocarbons, chiefly of the marsh-gas series (C_5H_{12}, C_6H_{14}), and homologous compounds." It is a transparent, colorless liquid, of neutral reaction, evaporating without residue and leaving no odor, of sp. gr. 0.670 to 0.675 at 15°, and boiling at 50° to 60° C. It is used as a solvent for fats, resins, rubber, and some of the alkaloids.

Petrolatum Liquidum, U. S. P., is stated to be "a mixture of hydrocarbons, chiefly of the marsh-gas series, obtained by distilling off the lighter and more volatile portions from petroleum, and purifying the residue when it has the desired consistence."

Petrolatum Molle, U. S. P., and **Petrolatum Spissum,** U. S. P., are both stated to be "mixtures of hydrocarbons, chiefly of the marsh-gas series, obtained by distilling off the lighter and more volatile portions from petroleum, and purifying the residue when it has the desired melting point." They are manufactured on the large scale under the trade names of vaseline, cosmoline, etc., by the filtration of oil residuums through heated bone-black.

The liquid petrolatum is a colorless or more or less yellowish, oily, transparent liquid, without odor or taste. It has a sp. gr. of 0.875 to 0.945 at 15° C.; the soft petrolatum, on the other hand, is a fat-like mass of about the consistence of an ointment, varying from white to yellowish or yellow, more or less fluorescent when yellow, especially after being melted, completely amorphous, and without odor or taste; and the hard petrolatum is a fat-like mass of about the consistency of a cerate, and in color like the softer variety. The melting point of the soft petrolatum is from 40° to 45° C., and of the hard variety from 45° to 51° C. All these varieties are insoluble in water, scarcely soluble in cold or hot alcohol, or in cold absolute alcohol, but soluble in boiling absolute alcohol, and readily soluble in ether, chloroform, carbon disulphide, oil of turpentine, benzine, benzene, and fixed or volatile oils.

Paraffinum Durum, B. P., is the solid commercial paraffine or paraffine wax, as it is often called. This is a white, waxy, inodorous, tasteless substance, of sp. gr. 0.877, melting (according to its source, whether from petroleum, coal, or ozokerite) between 43° and 65° C.

4. **Technically Important Products.**—The most important industry based upon the utilization of the hydrocarbons of this series is the refining of petroleum, which, as before stated, is a naturally occurring hydrocarbon mixture. In the United States the most important deposits of petroleum are those of Western Pennsylvania. These oil-fields extend into New York State and into Western Virginia and Ohio. In the latter State (as well as in

the province of Ontario, Canada) occurs also a petroleum deposit of somewhat different character, viz., a sulphur-containing oil, which presents greater difficulties in refining. Petroleum is also found in Kentucky, Colorado, and California, but of a heavier and thicker kind. The most important foreign production is that of Baku, on the Caspian Sea, where enormous quantities of petroleum are obtained. Chemically it differs, however, from the Pennsylvania oil in containing a distinct series of hydrocarbons, the so-called "naphthenes" (see Aromatic Hydrocarbons).

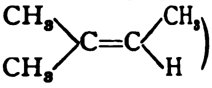
The refining of petroleum consists first in submitting it to a fractional distillation, the products of which are benzine, naphtha, burning oils, and residuum. The latter is then distilled at a higher temperature in separate stills, and yields paraffin oils and a coke or petroleum pitch. All the fractions require a treatment with sulphuric acid, followed by washing and treatment with alkali to remove impurities and products of destructive distillation, which impair their color and burning qualities. The paraffine oils are then chilled by artificial means and paraffine scale separated out from the heavy oils, which then are known as lubricating oils. The paraffine scale when purified by melting, pressing, and filtration yields the white paraffine wax.

The most important test to be applied to a burning oil is the "fire test," which determines the temperature to which it may be heated without liberating vapors which mixing with air may produce an explosive mixture. The lowest legal test in any of the States is 110° F., and in many it is placed at 150° F.

II. THE UNSATURATED HYDROCARBONS OF THE OLEFINE SERIES.

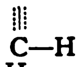
Associated with the paraffin series or saturated hydrocarbons in petroleum, and capable of being formed in most cases of destructive distillation, is a series of hydrocarbons each member of which contains two hydrogen atoms less than the corresponding member of the saturated series. They possess the general formula C_nH_{2n}.

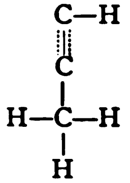
The first member of the series, CH_2, is apparently incapable of existing in the free state, although derivatives of it are known. The second hydrocarbon, C_2H_4, known as ethylene, the third, C_3H_6, known as propylene, and the succeeding ones as high as $C_{30}H_{60}$, are, however, obtainable. The explanation generally accepted by chemists for their molecular structure is that in them two carbon atoms are temporarily doubly linked, but that, as ant" (or oil-forming) gas. It combines with two atoms of hydrogen in the presence of spongy platinum to form ethane, C_2H_6.

Propylene and the several isomeric *butylenes* have been prepared. Of the *amylenes*, one (trimethyl-ethylene, ) has been introduced into medicine as an anæsthetic under the name of "pental." It is formed from tertiary amyl alcohol (amylene hydrate) by the action of dehydrating agents. It is a colorless, mobile, very volatile, and inflammable liquid, boiling at 37°–38° C. It is insoluble in water, but miscible in all proportions in chloroform, ether, and 90 per cent. alcohol.

III. THE UNSATURATED HYDROCARBONS OF THE ACETYLENE SERIES.

A third series of hydrocarbons, containing two hydrogen atoms less than the corresponding members of the olefine series and four less than the members of the paraffin series, is known under the name of the acetylene series. They have, therefore, the general formula C_nH_{2n-2}.

To explain their unsaturated character and their ability to take up four atoms of halogen or other atom or group, we assume the following structural formula for acetylene,  $\begin{array}{l}C—H\\ \;|||\\ C—H\end{array}$ or $CH\equiv CH$

and for the second member, allylene,  $\begin{array}{c}C—H\\ |||\\ C\\ |\\ H—C—H\\ |\\ H\end{array}$ or $CH\equiv C—CH_3$.

The first five members of this series are

Acetylene, C_2H_2,
Allylene, C_3H_4,
Crotonylene or Butine, C_4H_6,
Valerylene or Pentine, C_5H_8,
Hexine, C_6H_{10}.

They are produced in the destructive distillation of many organic compounds, such as wood and bituminous coal. Acetylene, the first member of the series, is produced in a variety of additional ways. Thus, when methane, ethane, ethylene, alcohol, ether, and aldehyde are led through tubes heated to redness, acetylene is produced with separation of hydrogen and other products. The incomplete combustion of many carbon compounds also causes the formation of acetylene, as in the case of defective gas-burners and in the use of gas-stoves. The most important reaction for its production, and at the same time the simplest, is the passage of the electric spark between carbon points in an atmosphere of hydrogen. We have here one of the simplest of organic syntheses, and from the acetylene so formed many other complex organic compounds can be built up.

Acetylene is a colorless gas with a peculiar penetrating odor, recognizable in cases of defective combustion with gas-burners. It burns with a luminous and smoky flame. Is soluble in water and alcohol. It is poisonous, combining with the hæmoglobin of the blood. It forms explosive compounds with potassium, sodium, silver, and copper, in which one or both hydrogen atoms are replaced by metal. It is capable of uniting with hydrogen when a mixture of the two is passed over heated platinum black, four atoms being taken up and ethane being formed.

IV. UNSATURATED HYDROCARBONS OF THE SERIES C_nH_{2n-4}. AND C_nH_{2n-6}.

In the distillation products of cannel coal, as well as in bone oil (Dippel's oil), are contained hydrocarbons of the series C_nH_{2n-4}. These are unsaturated, and take up six atoms of bromine by addition to form saturated compounds. They precipitate ammoniacal silver and copper solutions like acetylene.

Two hydrocarbons of this character have been described, *valylene*, C_5H_6, and *diallylene*, C_6H_8.

The terpenes, $C_{10}H_{16}$, which would answer to the general formula C_nH_{2n-4}, do not belong here, as they seem to be addition products of the aromatic compounds. They will, therefore, be considered after the discussion of these latter.

The only well-defined representative of the series C_nH_{2n-6} is *dipropargyl*, C_6H_6. This compound, isomeric with the aromatic hydrocarbon benzene, is an unsaturated open-chain hydrocarbon, as is shown by the readiness with which it adds on bromine and precipitates ammoniacal silver and copper salts.

CHAPTER III.

DERIVATIVES OF THE OPEN-CHAIN HYDROCARBONS.

I. HALOGEN DERIVATIVES.

1. Substitution Derivatives of the Paraffin Series.—Chlorine and bromine are capable of acting directly upon the hydrocarbons, replacing hydrogen. This action is facilitated by the presence of sunlight or substances which act as the "carriers" of the chlorine and bromine, such as iodine, ferric chloride, or antimony chloride. Iodine does not act directly upon the hydrocarbons, so that the iodides are generally obtained by the action of HI upon the several alcohols (see under Alcohols.)

TABULAR VIEW OF THE HALOID DERIVATIVES OF THE PARAFFINS.

Mono-Derivatives:	Boiling Point.
Monochlor-methane, or Methyl chloride, CH_3Cl	—22° C.
Methyl bromide, CH_3Br	+4°
Methyl iodide, CH_3I	44°
Monochlor-ethane, or Ethyl chloride, C_2H_5Cl	12°
Ethyl bromide, C_2H_5Br	39°
Ethyl iodide, C_2H_5I	72°
Propyl iodide, Isopropyl iodide, C_3H_7I	102°
Four isomeric varieties of Butyl iodide, C_4H_9I.	
Iso-amyl chloride, $C_5H_{11}Cl$	101°
Hexyl chloride, $C_6H_{13}Cl$	126°
Di-Derivatives:	
Dichlor-methane, or Methylene chloride, CH_2Cl_2	42°
Methylene bromide, CH_2Br_2	81°
Methylene iodide, CH_2I_2	180°
Ethylene chloride, $\left.\right\} C_2H_4Cl_2$	84°
Ethylidene chloride,	57°
Tri-Derivatives:	
Trichlor-methane, or Chloroform, $CHCl_3$	61°
Bromoform, $CHBr_3$	151°
	Melting Point.
Iodoform, CHI_3	119°
Higher Substitution Products:	
Tetrachlor-methane, or Carbon tetrachloride, CCl_4	77°
Perchlor-ethane, C_2Cl_6	185°

eral acceptance, perhaps because of its tendency to decompose with production of free bromine and hydrogen bromide.

Methylene Chloride, CH_2Cl_2, can be prepared by the action of chlorine upon methane or methyl chloride, or by the action of nascent hydrogen upon chloroform. It forms a colorless liquid with chloroform-like odor, boiling at 42°. It has been found to possess properties very similar to chloroform, producing an anæsthetic effect slightly more transient in character. This pure methylene chloride must not be confounded with a preparation brought out under the same name in England, which has been shown to be a mixture of 1 volume methyl alcohol and 4 volumes of chloroform.

Ethylene Chloride, $C_2H_4Cl_2$, is one of two isomeric compounds. It possesses the structural formula $CH_2Cl.CH_2Cl$, while its isomer, ethylidene chloride, has the formula $CH_3.CHCl_2$. Ethylene chloride is sometimes known as the "oil of the Dutch chemists," or simply as "Dutch liquid," because the reaction whereby it was formed by the direct union of ethylene and chlorine gases was first discovered in Amsterdam. It is a colorless liquid, of chloroform-like odor and sweet taste, and has been used as a substitute for chloroform both for external applications and for inhalations.

Ethylidene Chloride, $C_2H_4Cl_2$, is obtained as a by-product in the manufacture of chloral, or can be prepared by the action of phosphoric chloride upon paraldehyde. It is a colorless liquid, smelling like chloroform and of a sweet taste. It has been proposed by Liebreich as a substitute for chloroform in cases of anæsthesia.

Trichlor-methane, or **Chloroform**, U. S. P., $CHCl_3$, was discovered independently by Liebig and Soubeiran in 1831. Besides the preparation from methane by the action of chlorine, which is purely a theoretical process, we have three practical methods for its preparation.

(*a*) From alcohol by the action of chlorinated lime. This reaction most probably takes place in several stages. The chlorinated lime first oxidizes the alcohol to aldehyde according to the reaction :

$$C_2H_6O + CaOCl_2 = CaCl_2 + C_2H_4O + H_2O.$$

The aldehyde is then changed by the chlorinated lime into trichloraldehyde :

$$2C_2H_4O + 6(CaOCl_2) = 3CaCl_2 + 3Ca(OH)_2 + 2C_2HCl_3O.$$

The chloral thus formed is then decomposed by the alkaline calcium hydrate:

$$2C_2HCl_3O + Ca(OH)_2 = Ca(CHO_2)_2 + 2CHCl_3,$$

the end products being chloroform and calcium formate.

(*b*) From acetone by the action of chlorinated lime. This reaction, already pointed out by Liebig in 1832, has been taken up in recent years, and is now largely used in the manufacture of chloroform. It is as follows:

$$2C_3H_6O + 6CaOCl_2 = 2CHCl_3 + 2Ca(OH)_2 + Ca(C_2H_3O_2)_2 + 3CaCl_2.$$

(*c*) From chloral by the action of caustic alkalies, the reaction being analogous to that given under the first process.

Chloroform is a heavy, colorless, mobile, and diffusible liquid, of ethereal odor and burning, sweet taste. Specific gravity 1.49 at 15°. It boils at 60° to 61°. Chloroform is an excellent solvent for phosphorus, iodine, alkaloids, resins, caoutchouc, fats, fatty oils, etc. When exposed to the light it is liable to decomposition with liberation of hydrochloric acid and free chlorine, and hence must be kept in dark bottles. Its preserving qualities are improved by the addition of a small quantity of alcohol.

The most delicate chemical test for chloroform is the production of phenylcarbylamine, a compound of sickening odor when it is heated with alcoholic potash and aniline. One part of chloroform in 5000 to 6000 parts of solution can be detected in this way.

The most important medicinal use of chloroform is as an anæsthetic.

Tribromo-methane, or bromoform, $CHBr_3$, can be prepared from bromal by an analogous reaction to that used for preparing chloroform from chloral. It is a colorless liquid smelling like chloroform, and is somewhat used in medicine as an anæsthetic.

Triïodo-methane, or **Iodoform**, U. S. P., CHI_3, has been made most generally by the action of iodine in the presence of an alkali or alkaline carbonate upon alcohol, the main reaction being expressed as follows:

$$C_2H_5OH + 4I_2 + 3K_2CO_3 = CHI_3 + KCHO_2 + 5KI + 2H_2O + 3CO_2.$$

It is also made now by the action of iodine in the presence of an alkali upon acetone, the reaction being a very delicate one, serving to indicate traces of acetone, and known as the "iodoform test."

Iodoform is in small, lemon-yellow, lustrous crystals of the hexagonal system, with a peculiar, very penetrating and persistent odor, resembling saffron. The crystals melt at 119° C. They are very slightly soluble in water, soluble in alcohol, ether, chloroform, benzine, and fixed and volatile oils. It has a strong anæsthetic and antiseptic action, and is much used in surgery.

Tetrachlor-methane, or carbon tetrachloride, CCl_4, is a liquid boiling at 76.5° C.

Perchlor-ethane, C_2Cl_6, forms rhombic tablets of camphor-like odor. Fuse and boil at 185°.

2. **Halogen Derivatives of the Olefine Series.**—These may be either substitution derivatives, in which one or more H atoms of the unsaturated hydrocarbon are replaced by halogen, the double linking of carbon atoms characteristic of the olefines remaining unchanged, or they may be addition compounds, in which case two atoms of halogen add on. In the compounds so formed the unstable double linking is broken up, and the product is in all respects identical with the dihalogen substitution derivatives of the paraffins. Thus, from ethylene, C_2H_4, we may obtain C_2H_3Cl, monochlor-ethylene (vinyl chloride), and $C_2H_2Cl_2$, dichlor-ethylene, or we may get by addition $C_2H_4Cl_2$, ethylene chloride, already described under the preceding class. From propylene, C_3H_6, we may obtain C_3H_5Cl, monochlor-propylene (allyl chloride), representing the substitution derivatives, or $C_3H_6Cl_2$, propylene chloride, representing the addition compounds.

3. **Halogen Derivatives of the Acetylene Series.**—Here also both classes of compounds are possible,—substitution derivatives, in which the unstable treble linking still remains, and addition compounds, which pass into the class of olefine derivatives.

II. ALCOHOLS, OR HYDRATES OF THE HYDROCARBON RADICALS.

Alcohols are formed by the replacement of one or more hydrogen atoms of a hydrocarbon by the corresponding number of OH (hydroxyl) groups.

Alcohols with 1 hydroxyl group are termed *monatomic*, or monacid; alcohols with 2 hydroxyl groups are termed *diatomic*, or diacid; alcohols with 3 hydroxyl groups are termed *triatomic*, or triacid.

The highest of these classes as yet discovered in nature are the heptatomic alcohols, although higher ones have been obtained artificially. Two cases of isomerism may arise among the alcohols: (*a*) when they are derived from isomeric hydrocarbons; thus, from butane, $CH_3.CH_2.CH_2.CH_3$, we obtain normal butyl alcohol, $CH_3.CH_2.CH_2.CH_2OH$, and from isobutane, $\begin{matrix}CH_3\\CH_3\end{matrix}{>}CH{-}CH_3$, we obtain isobutyl alcohol, $\begin{matrix}CH_3\\CH_3\end{matrix}{>}CH{-}CH_2OH$; (*b*) according to the position taken by the replacing hydroxyl group; thus, while only one monatomic alcohol can be formed from methane, CH_4, and only one from ethane, $CH_3.CH_3$, from propane, $CH_3.CH_2.CH_3$, we can obtain normal propyl alcohol, $CH_3.CH_2.CH_2OH$, and isopropyl alcohol, $CH_3.CH.OH.CH_3$. Normal butane yields two isomeric alcohols, $CH_3.CH_2.CH_2.CH_2OH$ and $CH_3.CH_2.CH.OH.CH_3$, and isobutane yields two also, $\begin{matrix}CH_3\\CH_3\end{matrix}{>}CH{-}CH_2OH$ and $\begin{matrix}CH_3\\CH_3\end{matrix}{>}C(OH){-}CH_3$.

In looking at the formulas of these isomeric butyl alcohols it will be seen that we have three different types of monatomic alcohols: an alcohol containing the group $CH_2.OH$, known as a *primary* alcohol; an alcohol containing the group CH.OH, known as a *secondary* alcohol; an alcohol containing the group C(OH), known as a *tertiary* alcohol. We will find that these are important distinctions, as very different products are obtainable from the alcohols according as they belong to one or the other of these classes.

Secondary and tertiary alcohols are also known as *carbinols*, and the groups combined with the carbon atoms to which the hydroxyl is attached are specially named.

Thus, $\begin{matrix}CH_3\\CH_3\end{matrix}{>}C(OH){-}CH_3$ is called trimethyl-carbinol.

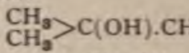
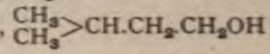
1. Monatomic Alcohols from Saturated Hydrocarbons.

General formula, $C_nH_{2n+1}.OH$.

TABLE.

Name and Formula:	Boiling Point.
Methyl alcohol, $CH_3.OH$	66° C.
Ethyl alcohol, $CH_3.CH_2OH$	78°
Normal propyl alcohol, $CH_3.CH_2.CH_2OH$	97°
Isopropyl alcohol, $CH_3.CHOH.CH_3$	83°
Normal butyl alcohol, $CH_3.CH_2.CH_2.CH_2OH$	117°
Isobutyl alcohol, $\begin{matrix}CH_3\\CH_3\end{matrix}{>}CH.CH_2OH$	108°
Methyl-ethyl carbinol, $\begin{matrix}CH_3.CH_2\\CH_3\end{matrix}{>}CHOH$	97°

TABLE.—*Continued.*

Name and Formula:	Boiling
Trimethyl carbinol,  $\begin{matrix}CH_3\\CH_3\end{matrix}>C(OH).CH_3$	83°
Normal amyl alcohol, $C_4H_9.CH_2OH$	137°
Fermentation amyl alcohol,  $\begin{matrix}CH_3\\CH_3\end{matrix}>CH.CH_2.CH_2OH$	131°
Hexyl alcohol, $C_6H_{13}.OH$	157°
Heptyl alcohol, $C_7H_{15}.OH$	175°
Octyl alcohol, $C_8H_{17}.OH$	191°
Nonyl alcohol, $C_9H_{19}.OH$	213°
	Melting
Decyl alcohol, $C_{10}H_{21}.OH$	7°
Dodecyl alcohol, $C_{12}H_{25}.OH$	24°
Tetradecyl alcohol, $C_{14}H_{29}.OH$	38°
Hexadecyl (cetyl) alcohol, $C_{16}H_{33}.OH$	49°
Octadecyl alcohol, $C_{18}H_{37}.OH$	59°
Ceryl alcohol, $C_{27}H_{55}OH$	79°
Myricyl alcohol, $C_{30}H_{61}.OH$	85°

The lower members of the series are mobile liquids solub
water, the middle members are oily liquids only slightly sc
in water, and the higher ones are solid crystalline bodies.
lowest members possess an alcoholic odor, those over C_5 an
of fusel oil, and both have a burning taste, while the hi
members are odorless and tasteless solids.

Among the general methods for the formation of alcohols
be mentioned:

(*a*) The action of moist silver oxide upon the haloge
rivatives of the paraffins, as $C_2H_5I + AgOH = C_2H_5.C$
AgI.

(*b*) The decomposition of the esters by boiling with c
alkalies. This decomposition is frequently spoken of a
"saponification" of the esters, because of the well-known
tration of the decomposition of the fats:

$$\underset{\text{Methyl Salicylate.}}{CH_3.OC_7H_5O_2} + KOH = CH_3.OH + \underset{\text{Potassium Sali}}{C_7H_5O_2.O}$$

(*c*) The treatment of primary amines with nitrous acid:

$$C_2H_5.NH_2 + NO.OH = C_2H_5.OH + N_2 + H_2O$$

(*d*) The fermentation of many of the carbohydrates (as
sugar) with yeast will produce the lower alcohols. (See Fe
tation.)

From ethylene and concentrated sulphuric acid and decomposition of the resulting ethyl-sulphuric acid by water:

$$C_2H_4 + SO_2(OH)_2 = C_2H_5.HSO_4.$$
$$C_2H_5.HSO_4 + H_2O = C_2H_5OH + H_2SO_4.$$

It is formed, however, almost invariably by the "alcoholic fermentation" of sugar. (See Fermentation.) The reaction whereby the sugar yields alcohol and carbon dioxide, $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$, is not a complete one, as some 5 per cent. of the sugar breaks up into other products, such as glycerin and succinic acid. A number of the homologues of ethyl alcohol are also formed, and are known collectively as "fusel oil."

While alcohol may be purified by repeated distillation, it is not possible to free it from water by this means. On a large scale in the several forms of rectifying columns it is possible to bring the alcohol to 98–99 per cent., but on the small scale to not over 95 per cent. The remaining portion of water must be taken out by chemical dehydrating agents, like heated carbonate of potash, anhydrous sulphate of copper, or standing, followed by a distillation over quick-lime. The alcohol thus obtained is the **Alcohol Absolutum, U. S. P.**

The presence of water in alcohol may be shown by admixture with benzene. This will mix to a clear liquid with alcohol containing not more than 3 per cent. of water. If the percentage begins to exceed this, the mixture becomes turbid. Anhydrous copper sulphate will also indicate the presence of water by changing from white to blue in color. Absolute alcohol boils at 78.5° C., becomes viscid at —100° C., and solidifies at —130°. Its specific gravity is 0.7937 at 15° C. It is very hygroscopic. Alcohol is a solvent for many organic compounds, such as fats, resins, and oils.

A very delicate test for alcohol (although not characteristic of alcohol only) is the iodoform test. The liquid to be tested is warmed with a small quantity of iodine dissolved in iodide of potassium solution, and sodium hydrate is added until the mixture is faintly yellow. In the presence of alcohol the characteristic smell of iodoform is obtained, and gradually the fine yellow crystals separate.

Benzoyl chloride, C_6H_5COCl, is also a delicate test for alcohol, with which it forms ethyl benzoate (benzoic ether), the smell of which is readily recognized. The commonest impurities of alcohol are aldehyde, which readily forms by oxidation, and fusel oil, which accompanies it in the products of fermentation. The former is detected by shaking up with a small quantity of potassium hydrate solution, whereby a brown aldehyde resin is formed; the latter is detected by evaporation of the suspected alcohol on the hand or from a piece of blotting-paper.

Besides alcohol (containing 94 per cent. by volume of ethyl alcohol) and alcohol absolutum, the United States Pharmacopœia recognizes **Alcohol Deodoratum** and **Alcohol Dilutum**, the latter containing about 48.6 per cent. by volume of absolute ethyl alcohol.

Alcohol has a dehydrating action upon vegetable and animal tissues. It coagulates albumen and prevents the decay of the tissue. Taken in small amount it has a slight stimulant effect; in larger doses it lowers the temperature and acts as an intoxicant, while in excessive amounts it is poisonous, and when injected into the veins it causes death. A portion of the alcohol taken into the system is burned to carbon dioxide and water; the remainder passes off through the lungs and the urine unchanged.

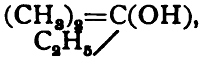
For an account of alcoholic beverages, see Fermentation Industries.

Propyl Alcohols, C_3H_7OH.—The normal propyl alcohol, $CH_3.CH_2.CH_2OH$, is contained in fusel oil, from which it may be obtained by fractionation. It may also be obtained by the action of sodium amalgam upon propion-aldehyde, or by the action of certain fissure ferments upon glycerin.

It is a liquid of spirituous odor, resembling that of methyl alcohol, boiling at 97.4°, and readily miscible with water, but can be separated out again by addition of calcium chloride. Isopropyl, or secondary propyl alcohol, $CH_3.CH(OH).CH_3$, may be obtained from isopropyl iodide (the product of the action of HI upon glycerin), or by the action of sodium amalgam upon acetone. Colorless liquid, boiling at 82.8°.

Butyl Alcohols, $C_4H_9.OH$.—The normal butyl alcohol, $CH_3.CH_2.CH_2.CH_2OH$, is present in fusel oil, being formed especially in the wine-yeast fermentation. It is also formed readily from glycerin by the fermentation with fissure ferments. It boils at 117°, and has a peculiar odor, inciting to coughing when inhaled. It is not so readily soluble in water, and may readily be separated out on addition of calcium chloride. Isobutyl alcohol, $\begin{matrix}CH_3\\CH_3\end{matrix}{>}CH.CH_2OH$, known frequently as fermentation butyl alcohol, is the most important of the butyl alcohols. It is contained in fusel oil, especially in potato fusel oil, and obtained in the beer-yeast fermentation. Colorless liquid, boiling at 108°, with a fusel smell, resembling that of wild jasmine.

Tertiary butyl alcohol, or trimethyl carbinol, $(CH_3)_3{\equiv}C(OH)$, is contained in small quantity in fusel oil. Spirituous smell resembling that of camphor. The remaining butyl alcohol, known as secondary butyl alcohol (see table), is only obtained synthetically.

Amyl Alcohols, $C_5H_{11}.OH$.—Of the eight possible isomeric alcohols, only four require mention. Normal primary amyl alcohol is contained in small quantity in fusel oil, and can be prepared by the reduction of normal valeric aldehyde. Its boiling point is 137°. Isobutyl carbinol, $(CH_3)_2{=}CH.CH_2.CH_2OH$, forms the chief constituent of fermentation amyl alcohol obtained from potato fusel oil. Is also found in Roman chamomile oil in combination with angelic and tiglic acids. It boils at 131°, and has a strong, irritating odor. It is intoxicating even in dilute solutions, and is the cause of the peculiar toxic after-effects of intoxication by brandy and other ardent spirits. It is optically inactive. Methyl-ethyl carbinol, or active amyl alcohol, is also contained in fermentation amyl alcohol. It turns the plane of polarization to the left. Boiling point, 112.5°. Tertiary amyl alcohol, or dimethyl-ethyl carbinol,  $\begin{matrix}(CH_3)_2{=}C(OH),\\ C_2H_5\diagup\end{matrix}$ has been introduced to medicine in recent years under the name of "amylene-hydrate," and recommended as an hypnotic. It is made from amylene, C_5H_{10} (see p. 564), by shaking this up with sulphuric acid, whereby amyl sulphuric acid, $SO_2\begin{cases}OH\\ O(C_5H_{11}),\end{cases}$ is formed. This, on distillation with aqueous alkalies, is decomposed into amylene hydrate and alkaline sulphate. The amylene hydrate is a colorless, oily liquid, of penetrating odor, which recalls camphor, peppermint, and paraldehyde. It boils at 102.5°, and has a specific gravity of 0.812 at 12°. It is soluble in 8 parts of water, and miscible in all proportions with alcohol, ether, chloroform, benzine, glycerin, and fatty oils. It is sensitive to light and very hygroscopic. As an hypnotic, it is said to occupy a position intermediate between chloral hydrate and paraldehyde.

Hexyl Alcohols, $C_6H_{13}.OH$.—The normal primary hexyl alcohol is contained as a butyric ester in the seeds of *Heracleum giganteum*. A primary hexyl alcohol is also obtained from wine fusel oil, and a secondary alcohol from mannite through the intermediate formation of secondary hexyl iodide.

Heptyl Alcohols, $C_7H_{15}.OH$.—The normal primary heptyl alcohol is obtained by the reduction of œnanthol, a normal aldehyde which forms on the distillation of castor oil.

Octyl Alcohol, $C_8H_{17}.OH$.—The normal primary octyl alcohol is found as an acetic ester in the several varieties of *heracleum*.

The normal primary alcohols, $C_{10}H_{21}.OH$, $C_{12}H_{25}.OH$, $C_{14}H_{29}.OH$, $C_{16}H_{33}.OH$, and $C_{18}H_{37}.OH$, were prepared artificially by Krafft, in 1881, by reducing the corresponding acids with zinc-dust and acetic acid. They are solids, like paraffin in appearance.

Cetyl Alcohol, $C_{16}H_{33}.OH$, formerly known as *ethal*, is found in combination with palmitic acid as the chief constituent of spermaceti (**Cetaceum**, U. S. P.). The alcohol crystallizes in small leaflets, fusing at 49° and boiling at 189.5°.

Octadecyl Alcohol, $C_{18}H_{37}.OH$, is also found in the form of esters in spermaceti.

Ceryl Alcohol, $C_{27}H_{55}.OH$, is found as cerotic ester in Chinese wax, and as palmitic ester in the ripe capsules of the poppy. The ceryl esters are also present in carnauba wax and in beeswax. The alcohol fuses at 76°–79°.

Myricyl Alcohol, $C_{30}H_{61}.OH$, is present as palmitic ester in beeswax and in carnauba wax, from which latter it is most conveniently extracted by saponification with alcoholic potash. The alcohol melts at 85° C.

2. **Monatomic Alcohols from Unsaturated Hydrocarbons**, $C_nH_{2n-1}.OH$.—These alcohols are derivatives of the olefine hydrocarbons, and, like them, contain the unstable double linking of two carbon atoms. They, therefore, like them, can take up two atoms of hydrogen or halogen element or one molecule of a haloid acid, forming thereby saturated alcohols, which may contain one or two replacing halogen atoms in the radical which is combined with the hydroxyl.

Vinyl Alcohol, $CH_2{=}CH.OH$, corresponding to Ethylene, $CH_2{=}CH_2$, has been found as an impurity in ordinary ether, but has not been isolated, as the isomeric acetaldehyde, $CH_3.CHO$, results in endeavoring to prepare it.

Allyl Alcohol, $CH_2{=}CH{-}CH_2OH$, corresponding to propylene, C_3H_6, is found in crude wood-spirit, and may be readily obtained by distilling glycerin with oxalic acid, the reaction being $C_3H_8O_3 - H_2O - O = C_3H_6O$, showing that the oxalic acid acts as a reducing and dehydrating agent. It is a mobile, colorless liquid, of penetrating, unpleasant odor, boiling at 96.6°, and miscible with water.

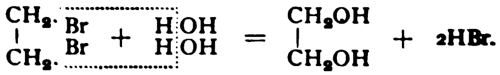
3. Monatomic Alcohols from Unsaturated Hydrocarbons, $C_nH_{2n-3}.OH$.—These alcohols are derivatives of acetylene and its homologues, and, like them, contain the unstable treble linking of two carbon atoms. They, therefore, can take up four atoms of hydrogen or halogen or two molecules of haloid acid to form saturated alcohols which may contain halogen atoms in the radical.

Propargyl Alcohol, $CH{\equiv}C{-}CH_2OH$, corresponding to allylene, C_3H_4, is obtained from monobromallyl alcohol by splitting off HBr, effected by the action of concentrated aqueous potash. Mobile, pleasant-smelling liquid, lighter than water, boiling at 114°.

4. Diatomic Alcohols or Glycols. General formula, $C_nH_{2n}(OH)_2$.—If two hydrogen atoms of a hydrocarbon of the paraffin series be replaced by two OH groups, we obtain a diatomic alcohol or glycol (from γλυκύς, sweet). Thus, from ethane, C_2H_6, we obtain ethylene glycol, $C_2H_4(OH)_2$. The two OH groups do not, however, attach to the same carbon atoms, so that, while theoretically both ethylidene glycol, $CH_3.CH(OH)_2$, and ethylene glycol, $CH_2OH{-}CH_2OH$, are possible, only the latter can be obtained. For this reason, also, the first of the series of glycols, methylene glycol, $CH_2(OH)_2$, cannot be obtained in the free state, although ethers corresponding to it are known. (See Methylal, p. 593.)

The distinction already noted under monatomic alcohols, of primary, secondary, and tertiary alcohols, of course exists here also, only, instead of three cases, six may arise, from the fact that there are the two replacing OH groups, the position of which is to be considered.

Glycols are formed most readily by forming first the dibromides of the hydrocarbons and then replacing the bromine atoms by hydroxyl groups. This can be effected by boiling the dibromides with water to which potassium carbonate or lead hydrate has been added to take up the hydrogen bromide liberated, the reaction being:



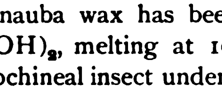
$$\begin{matrix} CH_2.Br \\ | \\ CH_2.Br \end{matrix} + \begin{matrix} H\,OH \\ H\,OH \end{matrix} = \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} + 2HBr.$$

They are also formed by the direct combination of the olefine hydrocarbons with hydrogen peroxide, or by oxidation of the olefines by potassium permanganate: $C_2H_4 + H_2O + O = C_2H_4(OH)_2$.

The glycols are mostly syrupy, sweet-tasting liquids of relatively high boiling point. They are readily soluble in water and alcohol, insoluble in ether. The double tertiary glycols, known specially as "pinacones," are, however, solid crystalline compounds.

Ethylene Glycol, $CH_2OH.CH_2OH$, is prepared from ethylene bromide, $C_2H_4Br_2$, and water in the presence of potassium carbonate. It is formed also along with trimethylamine on boiling an aqueous solution of cholin, a decomposition product of lecithin and protagon (see p. 803): $C_5H_{15}NO_2 = (CH_3)_3N + C_2H_4(OH)_2$. It is a sweetish, syrupy liquid, boiling at 197°.

Propylene Glycols, $C_3H_6(OH)_2$. — Two isomeric forms are known, α-propylene glycol, $CH_3.CH(OH).CH_2OH$, and β-propylene glycol, $CH_2OH.CH_2.CH_2OH$. The former of these can be prepared from propylene bromide, but is most easily obtained by distilling glycerin with caustic soda. It boils at 188°, and is converted by fissure ferments into a dextro- and a lævo-rotatory modification; the β-propylene glycol is also known as trimethylene glycol, and may be prepared from trimethylene bromide, or produced in the fissure fermentation of glycerin. It boils at 216°.

Hexylene Glycols, $C_6H_{12}(OH)_2$.—The most interesting compound of this formula is the so-called "pinacone," or tetramethyl-ethylene glycol,  $\begin{array}{l}C(OH)=(CH_3)_2\\ |\\ C(OH)=(CH_3)_2\end{array}$. It is most readily formed when acetone is reduced by metallic sodium in the presence of potassium carbonate. It forms a white, crystalline mass, with camphor-like odor, melting at 42° and boiling at 171°–172°. By oxidation it is reconverted into acetone.

Other glycols of high molecular weight are found in the natural waxes. Thus, from carnauba wax has been obtained a glycol of the formula $C_{25}H_{50}(OH)_2$, melting at 103.5°, and the white wax obtained from the cochineal insect under the name of *coccerin* on saponification yields *cocceryl alcohol*, $C_{30}H_{60}(OH)_2$.

5. Triatomic Alcohols, or Glycerins. General formula, $C_nH_{2n-1}(OH)_3$.—When three atoms of hydrogen in a hydrocarbon of the paraffin series are replaced by OH groups, we have a triatomic alcohol, or *glycerin*. Such alcohols act like triacid bases, and can combine with one, two, or three molecules of a monobasic acid.

The glycerins are colorless, syrupy liquids, readily soluble in water, and of high boiling point.

The first of the series, that derivable from methane, is unknown. Its formula, $CH(OH)_3$, would be too unstable to allow of its isolation, as a molecule of water would undoubtedly split off from the three OH groups here indicated as attached to the same carbon atom. Its ethyl ester, $CH(OC_2H_5)_3$, is, however, known under the name of orthoformic ether (see p. 586).

The second glycerin of the series corresponding to ethane is also unknown. Its formula, $C_2H_3(OH)_3$, also indicates that to one of the carbon atoms two OH groups would be attached, which gives us an unstable molecule. Its ethyl ester, $C_2H_3(OC_2H_5)_3$, is also known under the name of otho-acetic ether.

Propenyl Glycerin, $C_3H_5(OH)_3$ (**Glycerinum**, U. S. P.), is the triatomic alcohol corresponding to propane, and has the structural formula, $CH_2OH—CHOH—CH_2OH$. It occurs abundantly in nature in combination with the so-called fatty acids as esters of these latter, making up the bulk of the vegetable and animal fats and oils (see p. 621).

It is also produced in the alcoholic fermentation of sugar, and hence is found in most alcoholic beverages. It is also present in the urine as glycerin-phosphoric acid, a decomposition product of lecithin and protagon. It may be formed artificially by the action of water at 170° upon trichlorhydrin (trichlorpropane), $C_3H_5Cl_3$.

Practically, it is always obtained by the decomposition of the fats in connection with the manufacture of soaps and stearic acid. This decomposition may be effected by the aid of water in the form of superheated steam, by alkalies and metallic oxides, or by heating with sulphuric acid. For a fuller account of these methods, see section on Fat Industries.

The pure glycerin is a thick, colorless liquid, of specific gravity 1.27. It solidifies at low temperatures to monoclinic crystals, which fuse at 20° C. It boils at 290°, but in its ordinary impure state cannot be distilled at ordinary pressures without decomposition. It is very hygroscopic, and mixes with water and alcohol in all proportions. It is insoluble in ether, chloroform, carbon disulphide, benzine, benzene, and fixed or volatile oils. It is an excellent solvent for a great range of substances, such as bromine and iodine, alkaline chlorides, fixed alkalies, some of the alkaline earths, as lime, and a number of neutral salts. It also is said to have antiseptic properties.

obtained, however, in several cases by the reduction of certain *pentoses* (see Carbohydrates).

Arabite, $CH_2OH-(CH.OH)_3-CH_2OH$, has been prepared by the reduction of arabinose, $C_5H_{10}O_5$, with the aid of sodium amalgam. It fuses at 102°, and has a lævo-rotatory power in aqueous solution on the addition of borax.

Xylite, $C_5H_{12}O_5$, has been prepared by a similar method from xylose, $C_5H_{10}O_5$. It has not as yet been obtained crystalline, and is optically inactive.

Rhamnite, $C_6H_{14}O_5$, prepared from rhamnose, $C_6H_{12}O_5$, is a homologue of the foregoing. It fuses at 121°, and is right-rotatory in aqueous solution even without the addition of borax.

8. **Hexatomic Alcohols.** General formula, $C_nH_{2n-4}(OH)_6$. —Several alcohols of the formula $C_6H_{12}O_6$ have been found in nature, and have excited interest because of their close relation to one of the groups of carbohydrates or sugars. The nature of their relation and a method for the synthetic formation of them from these sugars have both been indicated in connection with the classic work of Emil Fischer on the Carbohydrates (see next page).

Mannite, $CH_2OH-(CHOH)_4-CH_2OH$, is found in many plants, as in the larch, in celery, in the leaves of *Syringa vulgaris*, in sugar-cane, in *Agaricus integer* (of the dry substance of which it forms 20 per cent.), in rye bread, and notably in the manna ash (*Fraxinus ornus*), the dried juice of which constitutes **Manna, U. S. P.**

Mannite crystallizes from water in thick rhombic prisms, or from alcohol in silky needles, melts at 165°–166°, is only moderately soluble in water, scarcely soluble in cold alcohol, and insoluble in ether. Its aqueous solution turns the plane of polarization very slightly to the left, but in the presence of borax and other salts it is strongly dextro-rotatory.

It has been obtained artificially by Fischer from both mannose and fructose (lævulose) by reduction with sodium amalgam in neutral or weakly acid solution ; when produced from fructose, sorbite, an isomeric alcohol, always accompanies it. Mannite is also formed from some of the sugars in the processes of fermentation, as in the lactic acid fermentation, and in especially large amount in the mucous fermentation of cane sugar.

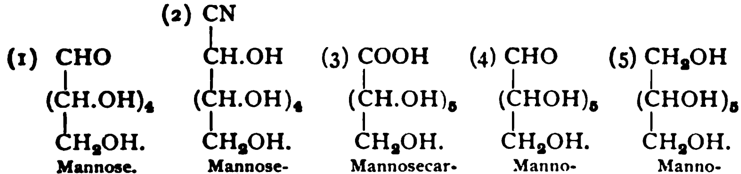
Fischer has shown that there are three mannites obtainable: the ordinary mannite is the dextro-rotatory variety, and is always obtained in the reduction of *a*-mannose ; a lævo-rotatory mannite is obtained by the reduction of *l*-mannose ; and an inactive mannite is obtained from the inactive mannose. The three varieties, besides differing in their optical characters, differ slightly in their fusing points and in their crystalline forms.

Sorbite, $C_6H_8(OH)_6$, is found in the berries of the mountain ash and in the fruit of the plum, cherry, apple, pear, etc. It crystallizes out of water in small, colorless needles, which contain water of crystallization. The anhydrous substance fuses at 110°–111°. It is slightly lævo-rotatory in simple aqueous solution, but in the presence of borax is dextro-rotatory. It has been prepared synthetically from dextrose, and represents the dextro variety of sorbite only, the lævo-sorbite having been also.

Dulcite (Melampyrite), $C_6H_8(OH)_6$, is found in certain plants like the *Melampyrum nemorosum*, but more particularly in the manna from Madagascar. It crystallizes in monoclinic prisms, fuses at 188.5°, and is still more difficultly soluble in water than mannite. Dulcite is optically inactive and not capable of being resolved into active modifications.

Rhamno-hexite, $C_7H_{10}(OH)_6$, a homologue of the preceding, has been prepared from rhamno-hexose, $C_7H_{14}O_6$. It crystallizes from hot alcohol in small, colorless prisms, melting at 173°, and is dextro-rotatory.

9. Heptatomic to Nonatomic Alcohols.—Starting with the group of sugars (hexoses) corresponding to the hexatomic alcohols, Emil Fischer has built up synthetically several alcohols of higher classes. Thus, the addition of hydrogen cyanide to a hexose will give what is termed a nitrile ; this when saponified yields an acid with seven carbon atoms, which can be reduced by sodium amalgam in successive steps to a sugar and a heptatomic alcohol. We may illustrate this in the case of mannose :



$$\begin{array}{ccccc}
 & (2)\ CN & & & \\
 & | & & & \\
(1)\ CHO & CH.OH & (3)\ COOH & (4)\ CHO & (5)\ CH_2OH \\
| & | & | & | & | \\
(CH.OH)_4 & (CH.OH)_4 & (CH.OH)_5 & (CHOH)_5 & (CHOH)_5 \\
| & | & | & | & | \\
CH_2OH. & CH_2OH. & CH_2OH. & CH_2OH. & CH_2OH.
\end{array}$$

Mannose. Mannose-cyanhydrin. Mannosecarboxylic Acid. Manno-heptose. Manno-heptite.

In this way an artificial alcohol, *δ-mannoheptite*, $C_7H_{16}O_7$, was prepared by Fischer, and later its identity with the naturally occurring *Perseite* was established.

Perseite is found abundantly in the fruits and leaves of *Laurus persea.* It crystallizes from water in microscopical needles, melting at 188°. Its aqueous solution alone is inactive, but on the addition of borax becomes strongly dextro-rotatory.

By analogous synthetical reactions to those given above, there has been obtained from mannoheptose an octatomic alcohol, ***δ-mannoctite***, $C_8H_{10}(OH)_8$. By the same method, starting from δ-glucose, there have been obtained the following synthetic alcohols: *α-glucoheptite*, $C_7H_{16}O_7$, fusing at 127°–128°; *α-glucooctite*, $C_8H_{18}O_8$, fusing at 141°; and *α-glucononite*, $C_9H_{20}O_9$, fusing at 194°.

III. ETHERS, OR OXIDES OF THE HYDROCARBON RADICALS.

The ethers may also be considered as the anhydrides of the alcohols. Thus, $2C_2H_5.OH = (C_2H_5)_2O + H_2O$. It may be, however, that two different alcohols can thus be united by the loss of one molecule of water. The resulting ether will then contain two different hydrocarbon radicals united by oxygen. Such a compound would be a mixed oxide. We distinguish, therefore, between the two classes, and have *simple ethers* or oxides of a single radical, and *mixed ethers* or oxides of mixed radicals. In both these cases, however, the radicals are obtained directly from the hydrocarbons by the loss of one or more hydrogen atoms, and are the same as unite with hydroxyl to form the alcohols. These alcohols, it will be remembered, were spoken of as basic hydrates, so the oxides will be basic oxides. Compounds where a basic or alcohol radical is united by oxygen to an acid radical used to be known as *compound ethers*, but, as they are really ethereal salts, they have been given the name of *esters*, to mark the distinction and to separate them clearly from the basic oxides or ethers.

We may distinguish between the ethers of the monatomic alcohols and those of higher alcohols.

1. Ethers of the Monatomic Alcohols.—These may be formed in several ways. By heating the alcohols with sulphuric acid the ethers can readily be obtained. The reaction goes on in two stages, however, as illustrated in the case of ethyl ether:

(*a*) $C_2H_5.OH + SO_2(OH)_2 = SO_2(OH).OC_2H_5 + H_2O$.
(*b*) $SO_2(OH)OC_2H_5 + C_2H_5.OH = C_2H_5.OC_2H_5 + SO_2(OH)_2$.

In the first reaction a compound known as ethyl-sulphuric acid (see p. 616) is formed, which then reacts with a second molecule of alcohol to form ethyl oxide or ether, and sulphuric acid is regenerated. Another general method for ether formation is to treat the halogen derivatives of the hydrocarbons with a sodium alcoholate or with alcoholic potash: $C_2H_5I + C_2H_5.ONa = C_2H_5.OC_2H_5 + NaI$.

The ethers are very stable. Ammonia, alkalies, dilute acids, and metallic sodium have no action upon them. They can be changed back into the corresponding alcohols by superheating with water in the presence of some acid, such as sulphuric.

Methyl Ether, $(CH_3)_2O$, is prepared from methyl alcohol and sulphuric acid. At ordinary temperatures is a gas, but can be changed by pressure or cold into a mobile liquid. Boils at —21° C., and burns with bluish flame.

Ethyl Ether, $(C_2H_5)_2O$ (**Æther**, U. S. P.), also known popularly as "sulphuric ether," because prepared by the aid of sulphuric acid. It is prepared by the reactions given above. As in these reactions the sulphuric acid is re-formed after serving to convert the alcohol into ether, it would seem as if the process might be kept up continuously. In fact, it is possible with small amounts of sulphuric acid to convert large quantities of alcohol into ether. The method is sometimes called the "continuous etherification process," but a limit is reached in the power of the sulphuric acid because side reactions interfere. Some sulphuric acid is reduced to sulphurous acid, and the slight impurities in the alcohol become carbonized. The temperature of the reaction must be kept as near 140° C. as possible, as at a higher temperature the acid acts dehydrating upon the alcohol, and at a lower temperature alcohol distils over unchanged. The product is washed with milk of lime to remove the sulphurous acid, then rectified, and the water and alcohol removed by chloride of calcium. The official ether is composed of about 96 per cent. by weight of absolute ether and about 4 per cent. of alcohol containing a little water.

To obtain absolute anhydrous ether, it must be treated with metallic sodium and again distilled.

Common ether is a transparent, mobile liquid, having a characteristic ethereal odor, and a burning, sweetish taste. Its specific gravity is 0.725 to 0.728 at 15° C., or 0.714 to 0.717 at 25° C. It boils at about 37° (the absolute ether boils at 34.97°) and melts at —117.4°. It is somewhat soluble in water (1 part in 10 parts water at 15° C.) and miscible in all proportions with alcohol, chloroform, benzine, benzene, fixed and volatile oils. Its vapor is very inflammable and forms an explosive mixture with air. Ether is a solvent for fats, resins, and many alkaloids; for bromine, iodine, phosphorus, and a number of salts. It is used in medicine largely as an anæsthetic.

In the manufacture of ether as carried out on a large scal side-products are obtained that may be mentioned. "Lig of wine" is obtained as a liquid, boiling between 150° and it is a mixture of ethers, ketones, and hydrocarbons. "H oil of wine," which boils above 300°, is a mixture of este sulphuric acid and olefine hydrocarbons.

Hoffmann's Anodyne (**Spiritus Ætheris Compositu** S. P.) is a mixture of ether, alcohol, and ethereal oil.

Methyl-ethyl Ether, $\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}O$, is an example of the r ethers. It is made most conveniently by the action of iodide upon sodium methylate :

$$C_2H_5I + NaOCH_3 = NaI + \left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right\}O.$$

Methyl-ethyl ether is a colorless liquid of peculiar odor, boils at 11° C. and is very inflammable. Compressed in form in cylinders it comes occasionally into use as an anæst being recommended by Richardson as a substitute for cl form.

Allyl Ether, $(C_3H_5)_2O$, is the oxide of the unsaturated r allyl and corresponds to allyl alcohol, $C_3H_5.OH$. It boils a

2. Ethers of the Diatomic Alcohols.—We may hav eral classes of compounds here, either the compounds of the radical and monad radicals like methyl and ethyl linked by gen, or the simple oxides of the dyad alcohol radicals. we have from $C_2H_4(OH)_2$, ethylene glycol, $C_2H_4\left\{\begin{matrix}OH\\OC_2H\end{matrix}\right.$ $C_2H_4(OC_2H_5)_2$, or C_2H_4O, which is simply ethylene oxide.

Ethylene Oxide, $\begin{matrix}CH_2\\CH_2\end{matrix}>O$, may be obtained by decomposir halogen derivatives of the glycols by aqueous alkalies. It i meric with acetaldehyde (see p. 590), but does not reduce ar niacal silver solution as does aldehyde. It is a strong base precipitates the hydrates of magnesium, aluminum, copper iron from the salts.

3. Ethers of the Triatomic and Tetratomic Alcoho While methenyl glycerin, $CH(OH)_3$, is unknown in the state, as stated before (see p. 580), its ethyl ether is kr The so-called *orthoformic ether*, $CH(OC_2H_5)_3$, is this comp Boiling point, 145°–146°. From propenyl glycerin or con glycerin, $C_3H_5(OH)_3$, we have similarly three ethers : $C_3H_5($ OC_2H_5, $C_3H_5(OH)(OC_2H_5)_2$, and $C_3H_5(OC_2H_5)_3$. The fi

The most important of the thio-ethers is:

Allyl Sulphide, $(C_3H_5)_2S$, known as "garlic oil," is obtained from the leaves of the garlic (*Allium sativum*) and the seeds of many of the Cruciferæ. It probably does not exist originally as such, but results as a decomposition product from more complicated materials. It boils at 140°. It can also be formed artificially from allyl iodide and potassium sulphide.

The sulphides of propyl, butyl, and amyl have recently been identified by Mabery as present in the crude petroleum of Lima, Ohio, and in Canadian petroleums.

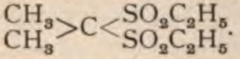
The sulphonic acids and salts contain the sulphonic group, HSO_3, combining directly, with the valence one, with the hydrocarbon radicals. They may be formed by boiling iodides of the hydrocarbon radicals with alkaline sulphites, $C_2H_5I + K_2SO_3 = C_2H_5KSO_3 + KI$, or by the oxidation of mercaptans, sulphides, and sulphocyanates with nitric acid, as before noted.

Methyl-sulphonic Acid, $CH_3.SO_3H$, has been prepared as a syrupy liquid.

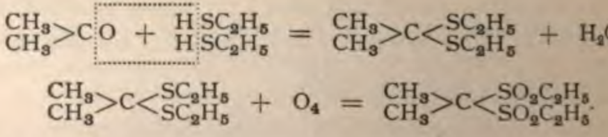
Ethyl-sulphonic Acid, $C_2H_5.SO_3H$, forms a deliquescent crystalline solid. A derivative of this, amido-ethyl-sulphonic acid, is known as *taurin*, and is present in the gall, in combination with cholic acid, as taurocholic acid.

Reference was made, under mercaptans, to the fact of their combining with ketones to form mercaptols. This reaction is a fundamental one in the preparation of the important product known as *sulphonal*.

Sulphonal (Diethyl-sulphone-dimethyl-methane),



$\begin{matrix}CH_3\\CH_3\end{matrix}>C<\begin{matrix}SO_2C_2H_5\\SO_2C_2H_5\end{matrix}$. This compound is prepared from ethyl mercaptan in two reactions. First, 2 molecules of the mercaptan unite with 1 molecule of acetone, with the elimination of water, to form the corresponding mercaptol. This is then oxidized by an acidified potassium permanganate solution. The reactions are:



$$\begin{matrix}CH_3\\CH_3\end{matrix}>C\boxed{O + \begin{matrix}H\\H\end{matrix}}\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix} = \begin{matrix}CH_3\\CH_3\end{matrix}>C<\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix} + H_2O.$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}>C<\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix} + O_4 = \begin{matrix}CH_3\\CH_3\end{matrix}>C<\begin{matrix}SO_2C_2H_5\\SO_2C_2H_5\end{matrix}.$$

Sulphonal forms colorless, odorless, and tasteless crystals, melting at 125°–126°, and boiling, with slight decomposition only, at 300°. More soluble in hot than in cold water; soluble in boiling alcohol. The solutions have a neutral reaction. If a small quantity of sulphonal be heated in a small test-tube with powdered charcoal, the characteristic odor of mercaptan is obtained. It is used very successfully as an hypnotic and soporific.

Trional (Diethyl-sulphone-methyl-ethyl-methane), $\begin{matrix}CH_3\\C_2H_5\end{matrix}>C<\begin{matrix}SO_2C_2H_5\\SO_5C_2H_2\end{matrix}$. If, instead of acetone (dimethyl-ketone), we take methyl-ethyl-ketone for the reaction with mercaptan, we obtain the product known as trional, which forms colorless, lustrous, and odorless crystals, melting at 76°, soluble in hot water, easily soluble in alcohol and ether. Its therapeutic action is similar to that of sulphonal, but it is said to act more rapidly and in smaller doses.

Tetronal (Diethyl-sulphone-diethyl-methane), $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>C<\begin{matrix}SO_2C_2H_5\\SO_2C_2H_5\end{matrix}$, is made by using diethyl-ketone (propione) instead of acetone for the reaction with mercaptan. It forms colorless, lustrous scales, which melt at 85°, easily soluble in boiling water and in alcohol, and moderately soluble in ether. It is very similar in its action to trional.

V. ALDEHYDES AND KETONES.

In speaking of these compounds under the head of Classification of Organic Compounds (see p. 552), they were referred to as products of oxidation of the alcohols. They are alike in this common derivation, but differ because of a fundamental difference in the alcohols from which they may be derived. Thus, if a primary alcohol containing the group $—CH_2OH$ is oxidized, it first loses two hydrogen atoms, and we have the group $—CO.H$, characteristic of aldehydes; if, on the other hand, a secondary alcohol containing the group $\overset{|}{\underset{|}{C}}H.OH$ is oxidized, it loses two hydrogen atoms, and we have the group $\overset{|}{\underset{|}{C}}O$, characteristic of ketones. Conversely, by the action of sodium amalgam upon aldehydes we get primary alcohols, while the action of the same reagent upon ketones gives us secondary alcohols. Another important difference between the two classes is, that aldehydes readily and in some cases spontaneously pass to a fuller stage of oxidation, viz., acids, in which the $—CO.H$ group is changed to a $—CO.OH$ group, while the ketones represent the final products of oxidation of the secondary alcohols.

They have some reactions in common and some which are distinctive of each class. Both aldehydes and ketones combine with alkaline bisulphites to form crystalline compounds, which, therefore, serve for their extraction and purification when admixed with other organic compounds. Both combine with hydrocyanic acid to form addition compounds known as *nitriles*, which, when saponified, yield acids by the change of the CN group to COOH. Both react with mercaptans (see p. 587). Both unite with hydroxylamine, $NH_2.OH$, to form *oximes*, known respectively as *aldoximes* and *ketoximes;* and both unite with hydrazines (see Phenylhydrazine, p. 703) to form a class of compounds called *hydrazones*.

The most important of the reactions which are characteristic of aldehydes alone are the reducing action upon ammoniacal silver solutions, whereby a silver mirror is obtained, and the formation of crystalline addition compounds with ammonia.

1. **Aldehydes of Saturated Alcohols.** General formula, $C_nH_{2n}O$.

Formaldehyde, HCO.H.—A mixture of gaseous methyl alcohol and air is led over gently-heated copper oxide, and the liquid obtained is carefully fractioned. It has been obtained as yet only as a gas of pungent odor, which reduces ammoniacal silver solution in the cold. It polymerizes very readily to form paraformaldehyde, $C_3H_6O_3$, a white, crystalline mass, or under other conditions to produce a substance known as "formose," from which Emil Fischer has isolated *α-acrose*, a sugar of the formula $C_6H_{12}O_6$.

Under the name of "Formalin" a 40-per-cent. aqueous solution of formaldehyde has been introduced into medicine. It is claimed for it that it is a non-poisonous antiseptic of great power, and as such has been used in surgical practice as well as for the preservation of foods and drinks.

Acetaldehyde, $CH_3.COH$.—This compound, obtained from common, or ethyl, alcohol, was first called aldehyde from *alcohol dehydrogenatum*, to indicate that its formula differed from that of alcohol in having lost two hydrogen atoms. It is found in both crude wood-spirit and grain-spirit, from the latter of which it can be obtained in the first running of the rectifying stills. It is most generally obtained, however, by the oxidation of ethyl alcohol with the aid of sulphuric acid and potassium dichromate or manganese dioxide. Ammonia gas is passed into an ethereal solution of this crude distillate, and the crystalline aldehyde-ammonia separated out. This compound is distilled with dilute sulphuric acid, when pure aldehyde can be collected. It is a colorless, mobile liquid, boiling at 21°, of a sharp and suffocating odor. In contact with a little hydrochloric or sulphuric acid or zinc chloride it quickly polymerizes and yields

Paraldehyde, $(C_2H_4O)_3$ (**Paraldehydum**, U. S. P.).—This is a colorless, transparent liquid, with a strong, characteristic, but not unpleasant odor, and a burning and cooling taste. It melts at 10° C., and boils at 123°–125°. It is soluble in 8.5 parts of water, and miscible in all proportions with alcohol, ether, and fixed or volatile oils.

Another polymeric form of aldehyde is *Metaldehyde*, $(C_2H_4O)_x$, which is produced from aldehyde at low temperatures, and is crystalline, subliming at 112°–115°. When heated to 120° under pressure it changes back to aldehyde.

By the action of chlorine upon alcohol chlorine substitution derivatives of aldehyde are formed, one, two, or three hydrogen atoms being replaced by chlorine. The most important of these derivatives is *Trichloraldehyde* (or Chloral), $CCl_3.COH$. This is an oily liquid, boiling at 98° C., of sharp, characteristic odor, which combines with sodium bisulphite, ammonia, and hydrogen cyanide like aldehyde, and like it reduces an ammoniacal silver solution. It crystallizes with one molecule of water to form

Chloral Hydrate (**Chloral**, U.S.P.), $CCl_3.COH + H_2O$.—The facts that chloral and water combine with development of heat, and that certain reactions given with chloral are not obtained with chloral hydrate, make it possible that this solid is not a mere hydrate, but a true chemical compound. It forms monoclinic crystals, fusing at 57° and boiling at 97°. It is freely soluble in water, alcohol, or ether; also in chloroform, benzine, benzene, carbon disulphide, and fixed and volatile oils.

Chloral is manufactured on a large scale by saturating ethyl alcohol with chlorine, first in the cold and afterwards with the aid of heat. After cooling there separates out a crystalline mass known as *chloral-alcoholate*, $CCl_3.CH{<}\begin{smallmatrix}OH\\OC_2H_5\end{smallmatrix}$. This is then heated with strong sulphuric acid, and when hydrochloric acid gas no longer escapes the chloral is distilled off. It is again rectified and mixed with the water necessary for the formation of the chloral hydrate. The action of chlorine upon alcohol is said to be aided by the presence of substances known as "chlorine carriers,'' like iodine. Ferric chloride also has been propo which case it is said that the chloral-alcoholate is not for an intermediate product.

One of the most important reactions of chloral is its position by alkalies and the resulting production of chlo according to the reaction: $CCl_3.COH + NaOH = CH$ $HCOONa$, whereby chloroform and sodium formate result purest chloroform is now made by this method from crys chloral hydrate. Chloral hydrate is an important hypno sedative.

Among the compounds of chloral that deserve mention of their proposed use in medicine are :

Chloral Cyanhydrate, $CCl_3.COH.HCN$, which forms crystalline masses, smelling like chloral hydrate, and mel 61°. This compound has been recommended for use ins bitter-almond water, as 6.46 grammes of it will contain un 1 gramme of anhydrous prussic acid.

Chloral Ammonium, $CCl_3.CH(OH)NH_2$, forms fine, needles, fusing at 82°–84°; nearly insoluble in cold wat composed by hot water, easily soluble in alcohol and ethe to be a good hypnotic and analgesic.

Chloralimide, $CCl_3.CH{=}NH$, differs from the preced the loss of the elements of water. Crystalline compound soluble in water, soluble in alcohol and ether. Used as notic.

Chloralformamide (*Chloralamide*), $CCl_3.CHO.HCON$ compound of chloral and formamide (see p. 631). It forms lustrous crystals, melting at 114°–115°; slowly soluble water, decomposed by hot water, readily soluble in Used as a soporific, being decomposed in the blood into and ammonium formate.

Chloralose, $C_8H_{11}Cl_3O_6$, is the name given to a compou tained by heating chloral and glucose, according to the re

$$CCl_3.CO.H + C_6H_{12}O_6 = C_8H_{11}Cl_3O_6 + H_2O.$$

It forms fine, colorless needles, melting at 184°–185° cultly soluble in cold water, more easily in warm water, soluble in alcohol. It is recommended as an hypnotic.

Chloral also combines with antipyrin in two proportio monochloral-antipyrine (or *hypnal*) and the bichloral-anti

Neither bromal, $CBr_3.COH$, nor iodal, $CI_3.COH$, has any use in medicine.

Butyraldehyde, $CH_3.CH_2.CH_2.COH$, results from the oxidation of butyl alcohol. It is also obtained by the oxidation of albuminoids by chromic acid. Its chlorine derivative :

Butyl Chloral, $C_4H_5Cl_3O$, also forms a hydrate which has been used in medicine as a substitute for chloral hydrate.

Œnanthaldehyde (Œnanthol), $C_7H_{14}O$, is an aldehyde obtained in quantity by the distillation of castor oil under reduced pressure, as the ricinoleic acid of the oil splits up, according to the reaction :

$$C_{18}H_{34}O_3 = C_7H_{14}O + C_{11}H_{20}O_2.$$

Œnanthol is a strongly refracting liquid of penetrating aromatic odor. Used in the manufacture of higher fruit ethers (see p. 617).

2. Aldehydes of Unsaturated Alcohols, $C_nH_{2n-2}O$.—These correspond to the unsaturated alcohols derived from the olefine hydrocarbons. They are, of course, unsaturated bodies also.

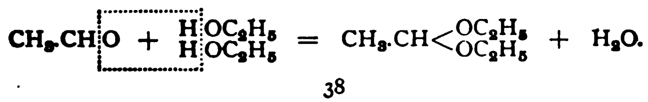
Acroleïn, $CH_2{=}CH.COH$, is the aldehyde corresponding to allyl alcohol, $C_3H_5.OH$. It is produced whenever glycerin is decomposed with loss of water; hence, in the superheating or distillation of the fats, as shown in the reaction $C_3H_5(OH)_3 - 2H_2O = C_3H_4O$. Liquid of sharp, irritating odor, causing tears, boiling at 52.4°.

Croton Aldehyde, C_4H_6O.—The next aldehyde in this series is found in the first runnings of raw spirits. Sharp-smelling liquid, boiling at 104°–105°. Reduces silver oxide, and is thereby oxidized to crotonic acid.

3. Acetals.—The acetals result from the union of alcohol with aldehydes with the elimination of water, or from the oxidation of the alcohols when they are produced along with the aldehydes.

Methylal, $HCH{<}\begin{smallmatrix}OCH_3\\OCH_3\end{smallmatrix}$, is obtained by oxidizing methyl alcohol with sulphuric acid and manganese dioxide, fractioning the product, and collecting the fraction boiling between 40° and 50°. Mobile, colorless liquid, of penetrating, aromatic odor, boiling at 42°. It is soluble in water, alcohol, ether, and fixed and ethereal oils. Used in medicine as an hypnotic.

Acetal, $CH_3.CH{<}\begin{smallmatrix}OC_2H_5\\OC_2H_5\end{smallmatrix}$, is formed by the reaction :

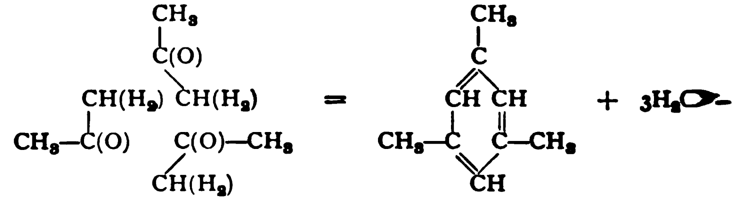


$$CH_3.CH\boxed{O + \begin{smallmatrix}H\\H\end{smallmatrix}}\begin{smallmatrix}OC_2H_5\\OC_2H_5\end{smallmatrix} = CH_3.CH{<}\begin{smallmatrix}OC_2H_5\\OC_2H_5\end{smallmatrix} + H_2O.$$

Is found also in the raw grain spirit when filtered through charcoal. Colorless liquid of agreeable taste, boiling at 104°, slightly soluble in water, very soluble in alcohol and ether.

4. **Ketones.**—The ketones are most readily distinguished from the aldehydes by their behavior to oxidizing agents. They are not affected by weak oxidizing agents; hence ammoniacal silver solution is not reduced by them as it is by aldehydes. Chromic acid and energetic oxidizing agents act upon them, but the ketone molecule is broken up thereby, and they yield acids with a smaller number of carbon atoms. Thus, acetone, $CH_3—CO—CH_3$, when oxidized yields acetic acid, CH_3COOH, CO_2, and H_2O.

The ketones show, like the aldehydes, a tendency to condense or polymerize. With acetone this condensation (by heating in the presence of concentrated sulphuric acid) gives rise to mesitylene, an aromatic hydrocarbon:



Dimethyl-ketone (Acetone), $CH_3—CO—CH_3$, is found in small amount in normal human urine, in the blood, and in secretions; the amount is notably increased in cases of disease like diabetes mellitus. It is contained in crude wood-spirit, and is a product of the distillation of sugar, gums, cellulose, etc. Technically it is obtained by the dry distillation of calcium acetate, according to the reaction:

$$\begin{matrix} CH_3.CO\vdots O \\ CH_3.\vdots COO \end{matrix}\Big> Ca = CH_3.CO.CH_3 + CaCO_3.$$

Is a liquid of ethereal, refreshing odor, boiling at 56° C. Soluble in water, alcohol, and ether. Sodium amalgam reduces it to isopropyl alcohol. A trace of acetone may be detected by the addition of a solution of iodine in potassium iodide along with an alkali, when iodoform is obtained, the odor and color of which are distinctive. Acetone is used largely as a solvent for resins, and in recent years in the manufacture of chloroform (see p. 569).

Methyl-ethyl Ketone, $CH_3.CO.C_2H_5$, is also contained in crude wood-spirit.

Methyl-nonyl Ketone, $CH_3.CO.C_9H_{19}$ is the chief constituent of oil of rue, from *Ruta graveolens*. Oil of pleasant odor, boiling at 224°. Yields on oxidation acetic and nonylic (pelargonic) acids, the latter of which is used in the manufacture of fruit ethers.

VI. Acids and Derivatives of Acids.

In speaking of the distinction between aldehydes and ketones (see p. 589), mention was made of the fact that aldehydes as the product of the oxidation of primary alcohols did not represent the final result of oxidation, but that the COH group of the aldehyde readily changed to a COOH group by a more complete oxidation. We may illustrate this by the example of ethyl alcohol: $CH_3.CH_2OH$, ethyl alcohol; $CH_3.COH$, acetaldehyde; CH_3COOH, acetic acid.

The group which is taken as characteristic of the acid is —CO.OH, known as "carboxyl," and the presence of one such group gives us a monobasic organic acid. If the alcohol contain two groups $—CH_2OH$, as in diatomic alcohols, the complete product of oxidation will contain two groups —COOH, and we shall have a dibasic acid.

The organic acids, like the alcohols, are hydrates,—that is, contain the OH group combined with a radical,—but they are acid hydrates instead of basic hydrates. Therefore the radical which is present combined with the —OH is spoken of as an acid radical, while the alcohol radical was a basic radical. We shall see that the acid radical always bears a very simple relation to the alcohol or basic radical from which it has been derived. What the difference is may be seen by comparing the formulas given above. Ethyl alcohol, CH_3CH_2OH, contains the radical *ethyl*, C_2H_5, combined with OH, while acetic acid, $CH_3.CO.OH$, contains the radical *acetyl*, CH_3CO, combined with OH. The acid radical we find to be formed from the alcohol radical by the exchange of two H atoms for an O atom.

1. Saturated Monobasic Acids (*Fatty Acid Series*), $C_nH_{2n}O_2$.—These are formed from the primary monatomic alcohols of the paraffin series by oxidation. They may also be formed from the cyanides of the hydrocarbon radicals next lower in the series by saponification, as in the reaction:

$$CH_3.CN + 2H_2O = CH_3.COOH + NH_3;$$

that is, methyl cyanide will yield acetic acid and ammonia. By this means we may pass up the series from one hydrocarbon or alcohol radical to the acid corresponding to the next hig drocarbon.

The higher members of this series of acids occur abu in nature, in the natural fats and oils combined with glyce in the waxes with monatomic alcohols as base, to form e salts.

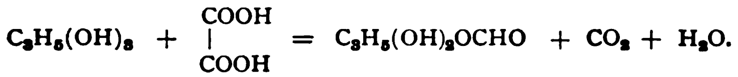
TABLE OF THE SATURATED MONOBASIC ACI (FATTY ACIDS).

Name.	Formula.	Melting Point.
Formic	$H.COOH$	9° C.
Acetic	$CH_3.COOH$	17°
Propionic	$CH_3.CH_2.COOH$	—24°
Butyric, Normal	$CH_3.(CH_2)_2.COOH$	0°
Butyric, Iso	$(CH_3)_2{=}CH.COOH$	Liquid.
Valeric, Normal	$CH_3.(CH_2)_3.COOH$	Liquid.
Valeric, Iso	$(CH_3)_2{=}CH.CH_2.COOH$	Liquid.
Methyl-ethyl-acetic	$\begin{matrix}CH_3\\C_2H_5\end{matrix}{>}CH.COOH$	Liquid.
Trimethyl-acetic	$(CH_3)_3{=}C{-}COOH$	35°
Caproic	$C_6H_{12}O_2$	—2°
Œnanthic	$C_7H_{14}O_2$	—10°
Caprylic	$C_8H_{16}O_2$	16°
Pelargonic	$C_9H_{18}O_2$	12°
Capric	$C_{10}H_{20}O_2$	31°
Undecylic	$C_{11}H_{22}O_2$	28°
Lauric	$C_{12}H_{24}O_2$	44°
Tridecylic	$C_{13}H_{26}O_2$	40°
Myristic	$C_{14}H_{28}O_2$	54°
Pentadecylic	$C_{15}H_{30}O_2$	51°
Palmitic	$C_{16}H_{32}O_2$	62°
Margaric	$C_{17}H_{34}O_2$	60°
Stearic	$C_{18}H_{36}O_2$	69°
Nondecylic	$C_{19}H_{38}O_2$	66°
Arachidic	$C_{20}H_{40}O_2$	77°
Behenic	$C_{22}H_{44}O_2$	76°
Lignoceric	$C_{24}H_{48}O_2$	80°
Cerotic	$C_{27}H_{54}O_2$	78°
Melissic	$C_{30}H_{60}O_2$	90°

* Boiling points under a pressure of 100 mm.

Formic Acid, HCO.OH, was first obtained from the b ants (*Formica rufa*), whence the name. It also occurs bristles of the stinging nettle, the fruit of the soap-tree, tamarinds and fir-cones ; also in perspiration, urine, and t of flesh. It is made artificially by a variety of reaction of which are direct syntheses from inorganic materials. the action of moist carbon monoxide upon dry sodium (or, better, granular soda-lime) at temperatures of 160°–20 give us a rapid and abundant production of sodium formate: $CO + NaOH = HCO.ONa$.

It may also be obtained by the oxidation of methyl alcohol; by the reaction of water upon hydrogen cyanide in the presence of acids or alkalies, according to the reaction $HCN + 2H_2O = HCOOH + NH_3$; by the decomposition of chloroform and chloral by alkalies; or, finally, by the heating of oxalic acid in the presence of glycerin. This method is the one usually employed, as the glycerin is regenerated and so can convert large quantities of oxalic acid into formic acid. The reactions are:



$$C_3H_5(OH)_3 + \begin{array}{c}COOH\\ |\\ COOH\end{array} = C_3H_5(OH)_2OCHO + CO_2 + H_2O.$$

$$C_3H_5(OH)_2OCHO + H_2O = HCOOH + C_3H_5(OH)_3.$$

Formic acid is a colorless liquid with penetrating odor. The liquid produces a painful inflammation if dropped upon the skin, but acts as a powerful antiseptic in dilute solution. Formic acid in solution may be recognized by the reducing power it exerts upon silver and mercury salt solutions. Thus, metallic silver is separated out on heating formic acid with silver nitrate solution, while white calomel is separated out on adding formic acid to corrosive sublimate solution. Formic acid unites with inorganic bases to form salts called *formates*, all of which are easily soluble except the lead and mercurous salts. The formates containing organic bases will be spoken of under "Esters."

Acetic Acid, $CH_3.COOH$, was known to the ancients in the form of wine vinegar, and in a purer and more concentrated form to the alchemists. It is found partly free and partly combined with potassium and calcium in various plant juices, and in the perspiration, milk, urine, muscles, and excrementa of animals. It results from the fermentative decomposition of albuminoids and glue, and the dry distillation of wood, starch, and sugar. A complete synthesis of it has been accomplished by the oxidation of acetylene, which (see p. 565) can be built up from carbon and hydrogen. Thus, $CH{\equiv}CH + H_2O + O = CH_3COOH$.

The two great sources of acetic acid, however, are the acetic fermentation of alcoholic liquids (see Fermentation), and the dry distillation of wood. As made from this latter source it is known as "pyroligneous" acid, and is quite impure from the presence of creosote and other empyreumatic products found in wood-tar. It is purified by neutralizing with milk of lime, whereby the "brown acetate of lime" is obtained. This is purified by roasting off the tarry impurities, decomposed with hydrochloric acid, and the acetic acid distilled off. It may be further purified by the recrystallization of the sodium salt.

Acetic acid when pure is a strongly acid liquid of pungent odor, burning the skin, and solidifying in the cold to crystalline plates, melting at 17°, and boiling at 118°, sp. gr. at 15° 1.055. This is known as glacial acetic acid (**Acidum Aceticum Glaciale**, U. S. P.). Two other strengths of acid are also official, one containing about 36 per cent. by weight of absolute acetic acid (**Acidum Aceticum**, U. S. P.), and a still more dilute acid containing 6 per cent. by weight of absolute acetic acid (**Acidum Aceticum Dilutum**, U. S. P.).

The glacial acetic acid has a strong solvent power for many organic substances, and hence is frequently used as a solvent from which to crystallize out organic preparations. Acetic acid may be detected by first neutralizing with ammonia and then adding ferric chloride, when a blood-red color of ferric acetate is obtained, which color is destroyed by heating with hydrochloric or sulphuric acids, or by heating with alcohol and sulphuric acid, when the characteristic odor of acetic ether is obtained.

The salts of acetic acid are known as *acetates*. All the neutral salts are soluble in water, but insoluble basic acetates of several of the heavy metals are obtained. The official metallic acetates are:

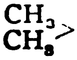
Potassii Acetas, U. S. P., $KC_2H_3O_2$.—A white, deliquescent salt, odorless, and of a saline taste, readily soluble in water and alcohol.

Sodii Acetas, U. S. P., $NaC_2H_3O_2+3H_2O$. — Colorless, monoclinic prisms, odorless, and of saline taste, efflorescing in dry air. Soluble in water, less readily soluble in alcohol.

Plumbi Acetas, U. S. P., $Pb(C_2H_3O_2)_2 + 3H_2O$.—Forms colorless, shining, transparent, monoclinic prisms, with faintly acetous odor, and a sweetish, astringent, and metallic taste. Efflorescent, and absorbing carbon dioxide in air, easily soluble in water, and moderately soluble in alcohol.

Zinci Acetas, U. S. P., $Zn(C_2H_3O_2)_2+2H_2O$.—Soft, white monoclinic plates, of pearly lustre, faintly acetous odor, and astringent, metallic taste. Gradually effloresces in the air. Easily soluble in water, moderately soluble in alcohol.

Besides these crystalline salts, we have several acetates official in solution, as **Liquor Ammonii Acetatis**, U. S. P.;

Isovaleric acid,  $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\!>CH.CH_2COOH$, is found abundantly in dolphin oil and in the root of *Valeriana officinalis*. It is also found in human excrement, and is a product of the decomposition of albuminoids, hence its occurrence in old cheese. It may be obtained most readily by the oxidation of the amyl alcohol of fermentation by the aid of sulphuric acid and potassium bichromate. Liquid of strong, unpleasant odor of valerian, boiling at 175°. Several of the metallic valerianates are of importance in medicine. These are:

Ammonii Valerianas, U. S. P., $NH_4C_5H_9O_2$.—Colorless, crystalline plates, with the odor of valerian, of a sharp, sweetish taste, and deliquescent in moist air. Soluble in water, alcohol, and ether.

Ferri Valerianas, U. S. P.—Forms a dark brick-red, amorphous powder, with the odor of valerian, and a mild, styptic taste; permanent in dry air.

Zinci Valerianas, U. S. P., $Zn(C_5H_9O_2)_2+2H_2O$.—White, pearly scales, having the odor of valerianic acid, and a sweetish, astringent, and metallic taste. Not very soluble in water, more soluble in alcohol.

The other varieties of valeric acid are only of theoretical interest as yet.

Caproic Acid, $C_6H_{11}O.OH$.—The normal caproic acid is found in cocoanut oil and Limburg cheese, and is produced in the butyric fermentation of sugar and the oxidation of albuminoids, and as glycerin ester in butter made from goat's milk. Like valeric acid, it has a very persistent and unpleasant odor of perspiration and rancid butter.

Caprylic Acid, $C_8H_{15}O.OH$, is found, with caproic and capric acids, in the butter from goat's milk (whence the names), and in butter, cheese, and wine fusel oil.

Pelargonic Acid, $C_9H_{17}O.OH$, is found among the volatile constituents of the plant *Pelargonium roseum*.

Lauric Acid, $C_{12}H_{24}O_2$, is contained as glyceride in the oil from *Laurus nobilis*, as well as in cocoanut oil, pichurim beans, dika bread, and in spermaceti.

Myristic Acid, $C_{14}H_{28}O_2$, is contained in nutmeg butter and in oil of iris. Small quantities have also been found in butter and in spermaceti.

Palmitic Acid, $C_{16}H_{31}O.OH$, is found abundantly in combination with glycerin as an ester "palmitin" (see p. 619). The acid is distilled with oxide of lead. Unpleasant, acrid, and penetrating smelling liquid. Crystallizes when cooled. Boiling point 140° ; easily soluble in water.

Crotonic Acid, $C_4H_6O_2$.—Three isomeric varieties are known, of which the first and the second occur in crude pyroligneous acid, while the third is found in Roman chamomile oil.

Angelic Acid and *Tiglic Acid*, $C_5H_8O_2$.—The former of these isomeric acids is found in angelica root as well as in Roman chamomile oil, where it is present as an ester ; the latter, also, in the Roman chamomile oil as amyl ester.

Hypogæic Acid and *Physetolic Acid*, $C_{16}H_{30}O_2$.—The former of these isomeric acids is found in the fruit of the earth-nut (*Arachis hypogæa*) as glyceride, and forms crystals, melting at 33° ; the latter is found in sperm oil (from the head of *Physeter macrocephalus*), and melts at 30°. The first acid yields, on distillation, sebacic acid, while the second does not yield this product ; the first is changed by nitrous acid into an isomeric modification, the second is not affected by nitrous acid.

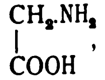
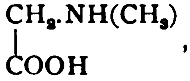
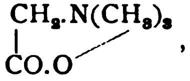
Oleic Acid, $C_{18}H_{34}O_2$ (**Acidum Oleicum**, U. S. P.), is found abundantly in nature as glyceride in all the fat oils, both vegetable and animal. A colorless oil, forming white needles when chilled. Melting point 14°. The oil has a sp. gr. of about 0.900 at 15° C. It is insoluble in water, soluble in alcohol, chloroform, benzene, benzine, oil of turpentine, and fixed and volatile oils. It cannot be vaporized without decomposition. A small quantity of nitrous acid changes it into the isomeric *Elaidic acid*, which is white and crystalline, fusing at 45°.

Döglinic Acid, $C_{19}H_{36}O_2$, found as glyceride in the oil of *Balæna rostrata* (dögling whale). Oil solidifying at low temperatures.

Erucic Acid, $C_{22}H_{42}O_2$, is found in black and white mustard seed oil. It forms needles melting at 33°–34°. With a small quantity of nitrous acid, is changed into the isomeric *brassidic acid.*

3. **Unsaturated Monatomic Acids** (*Propiolic Acid Series*). $C_nH_{2n-4}O_2$.—The acids of this series correspond to the acetylene hydrocarbons, and are capable of adding on four atoms of halogens like iodine. They may be formed by the direct addition of carbon dioxide to the sodium compounds of the acetylene hydrocarbons, as :

$$\underset{\text{Acetylene-sodium.}}{CH{\equiv}CNa} \quad + \quad CO_2 \quad = \quad \underset{\text{Propiolate of Sodium.}}{CH{\equiv}C.COONa.}$$

glue or silk with alkalies or acids, by the decomposition of hippuric acid (see p. 720) with hydrochloric acid, or by heating monochloracetic acid with ammonia. It forms large, colorless, rhombic prisms, easily soluble in water, insoluble in absolute alcohol and ether; melts with decomposition at 232° to 236°. As an amido-acid it unites in itself both the properties of a base and an acid. It forms a hydrochlorate on the one hand, and a well-crystallized copper salt on the other. Substitution derivatives from glycocoll are also obtained by the replacement of the hydrogen of the amido group. Thus, from glycocoll,  $\begin{array}{l}CH_2.NH_2\\|\\COOH\end{array}$, we obtain methyl-glycocoll, or *sarcosine*,  $\begin{array}{l}CH_2.NH(CH_3)\\|\\COOH\end{array}$, which is a decomposition product of creatine and caffeine (see p. 667), and trimethyl-glycocoll, or *betaine*,  $\begin{array}{l}CH_2.N(CH_3)_3\\|\quad\diagup\\CO.O\end{array}$, which is contained in beet-root and cotton-seed, and is related to choline.

Amido-propionic Acid, $CH_3.CH\ (NH_2).COOH$, is also known as "alanine." It can be obtained by the action of dilute acids upon silk or the action of hydrocyanic acid upon aldehyde-ammonia. Hard needles of sweetish taste.

Amido-butyric Acid, $NH_2.(CH_2)_3.COOH$.—One of the amido-butyric acids is piperidinic acid, which results from the oxidation of piperyl-urethan.

Amido-valeric Acid, $NH_2(CH_2)_4.COOH$.—One of the amido-valeric acids has been obtained in the decomposition of fibrin and flesh, and of conine and piperidine derivatives, and has also been found in the pancreas of the ox.

Amido-caproic Acid, $C_5H_{10}(NH_2)COOH$.—This important substance is known also as "leucine," and is found widely spread in both animal and vegetable material. It is found in old cheese, in the animal organism in the gastric salivary gland, and along with tyrosine is a constant product of the digestion of albumen in the small intestine and of the decay of albuminous substances; it is also found in the shoots of the vetch and the gourd. Most conveniently made by boiling clippings of horn with dilute sulphuric acid. Forms scales soluble in water, difficultly soluble in cold, more readily soluble in hot alcohol. Leucine is dextro-rotatory, but is made inactive by heating with baryta water.

inactive ethylidene-lactic acid (lactic acid of fermentation) and the active ethylidene-lactic acid (sarco-lactic acid).

Fermentation lactic acid (**Acidum Lacticum,** U. S. P.) occurs in opium, sauerkraut, the gastric juice, and the gray matter of the brain. It is produced by the lactic fermentation of sugar (see p. 656), and hence contained in such products as sour milk, koumiss, kefir, etc. The official lactic acid contains 75 per cent of absolute lactic acid, and is a colorless, syrupy liquid, odorless, of acid taste, and sp. gr. about 1.213 at 15°. It is hygroscopic, and freely miscible with water, alcohol, or ether; insoluble in chloroform, benzine, or carbon disulphide. Lactic acid when heated in dry air gives rise to characteristic anhydrides. Thus, $2C_3H_6O_3 - H_2O = C_6H_{10}O_5$, *Lactic Anhydride*, and this at a higher temperature again loses a molecule of water, yielding *Lactide*, $C_6H_8O_4$, a stable compound crystallizing in colorless tablets, melting at 125°, and boiling undecomposed at 255°. The official metallic lactates are:

Ferri Lactas, U. S. P., $Fe(C_3H_5O_3)_2 + 3H_2O$. — This salt is in pale, greenish-white crusts or needle-shaped crystals, with a slight, peculiar odor, and a mild, sweetish, ferruginous taste. Slowly but completely soluble in water, almost insoluble in alcohol, freely soluble in solutions of alkaline citrate.

Strontii Lactas, U. S. P., $Sr(C_3H_5O_3)_2 + 3H_2O$.—A white, granular or crystalline compound, odorless, and of a slightly bitter, saline taste. Permanent in air. Soluble in water and alcohol.

Sarco-lactic (or Para-lactic) acid is found in the muscles (hence also in extract of beef), in the blood, and in the urine after strong muscular exertion. It is the dextro-rotatory modification, and can be produced together with the lævo-rotatory modification by splitting up the inactive or ordinary lactic acid. This is accomplished by the fractional crystallization of the strychnine salt.

Ethylene-lactic (or Hydracrylic) acid forms a syrupy mass. It differs from ordinary lactic acid in yielding carbonic and oxalic acids on oxidation instead of acetic acid, and in not yielding an anhydride on heating, but breaking up into water and acrylic acid, whence the name hydracrylic.

Oxybutyric Acid, $C_3H_6OH.COOH$. — An optically active (lævo-rotatory) modification of this acid is found in the urine and the blood of diabetic patients.

The dibasic acids result when the diatomic alcohols are oxidized with nitric acid or by the saponification of the cyanogen derivative of the fatty acids.

Pyrotartaric Acid, $COOH.C_3H_6.COOH$.—Of the several isomeric forms, the most important are glutaric acid, the normal pyrotartaric acid, which is found in suint of sheep's wool and in juice of the beet-root, and methyl-succinic acid.

Of the higher acids of this series may be mentioned *Adipic Acid*, $(CH_2)_4.(COOH)_2$, obtained by the oxidation of the fats by nitric acid ; *Suberic Acid*, $C_8H_{14}O_4$, obtained by the action of nitric acid upon cork tissue ; *Sebacic Acid*, $C_{10}H_{18}O_4$, obtained by the dry distillation of spermaceti and fats containing oleic acid ; and *Rocellic Acid*, $C_{17}H_{32}O_4$, found in the lichen *Rocella fuciformis*.

From unsaturated alcohols containing two $CH_2.OH$ groups may also be prepared acids which will, of course, show the unsaturated character. They bear to the acids just described the same relation that the oleic acid series does to the fatty acid series. They have the general formula $C_nH_{2n-4}O_4$. The most important are :

Fumaric and *Maleic Acids*, $C_2H_2(COOH)_2$.—The first of these isomeric acids is found in *Fumaria officinalis*, in mushrooms, and in Iceland moss. It is formed from malic acid by the loss of water, and from albuminoids by the action of aqua regia. Under the influence of nascent hydrogen, it takes up two H atoms and yields succinic acid. When heated strongly for a time it changes into the isomeric maleic acid. This acid may also be obtained by the distillation of malic acid. It is more soluble in water than fumaric acid.

6. Acids derived from Triatomic and Higher Alcohols.—No matter what the number of OH groups contained in the alcohols, whether three, as in the glycerins, or four, five, or six, the presence of a group, CH_2OH, gives rise to the acid character in the products of oxidation, and the basicity of the acid depends upon the number of the $CH_2.OH$ groups so changed to COOH.

Glyceric Acid, $CH_2OH.CHOH.COOH$, results from the careful oxidation of glycerin with nitric acid, and is obtained also in the spontaneous decomposition of nitroglycerin. Syrup, soluble in water and alcohol.

Tartronic Acid, $COOH.CHOH.COOH$, results from the oxidation of glycerin with potassium permanganate. Prismatic crystals easily soluble in water and alcohol, difficultly soluble in ether. Melting point 185°.

Malic Acid, $COOH.CH_2.CHOH.COOH$, known also as oxysuccinic acid, is very widely distributed in the vegetable king-

dom, being found in unripe apples, quinces, grapes, ba
etc. It may be formed also from succinic acid, on the o
by replacing an H atom by OH, or from tartaric acid
other hand, by reduction with HI.

It forms hygroscopic needles, easily soluble in water a
hol, only slightly soluble in ether. Melting point 100°.
to 120°–130 it yields fumaric acid, and at 175°–180° m
is formed.

The amides and amines of malic acid will be considered fa

Tricarballylic Acid, $C_3H_5.(COOH)_3$, occurs in unrip
and is prepared synthetically from glycerin through th
vention of the bromine and cyanogen compounds of the
radical, C_3H_5. Its relations to citric and aconitic acids
from the table, and it can be formed from both by simp
tions. It forms prisms, melting at 166°, soluble in wate

Aconitic Acid, $C_3H_3(COOH)_3$, is an unsaturated aci
found in nature in *Aconitum napellus*, *Achillea millefo*
the sugar-cane, and the beet-root. It is also readily prep
quick heating of citric acid, when a molecule of H_2O s
It forms crystals, melting at 186°. Easily soluble in wat

Erythritic Acid, $C_3H_4(OH)COOH$, is formed by th
tion of erythrite with nitric acid or platinum black.

Tartaric Acid, COOH.CHOH.CH.OH.COOH (
Tartaricum, U. S. P.), is sometimes known also as di
cinic or oxy-malic acid, in order to indicate its relations
well-known acids. Tartaric acid exists in four *physically*
modifications : dextro-tartaric, lævo-tartaric, racemic or
tartaric, and meso-tartaric. The first of these is the
occurring variety. It occurs partly free and partly as p
or lime-salt in the juice of the grape and other fruits.
potassium tartrate which is found in the grape juice
insoluble as fermentation proceeds, and the liquid becom
holic and separates as "argols" in the wine-casks.
purified by conversion into the lime-salt from which th
liberated with H_2SO_4. The pure acid forms colorless,
clinic prisms or white powder, with an acid taste, and pe
in the air. Is soluble in water and alcohol, difficultly s
ether, nearly insoluble in chloroform, benzene, or
Melting point 135°. It reduces an ammoniacal silver
upon warming. When strongly heated, carbonizes an
off a characteristic "caramel" odor. The most impor
trates are :

Neutral Potassium Tartrate, $K_2C_4H_4O_6+\frac{1}{2}H_2O$, which forms monoclinic prisms easily soluble in water.

Acid Potassium Tartrate, $KHC_4H_4O_6$, or **Potassii Bitartras,** U. S. P.—This compound, known also as "cream of tartar," forms small rhombic crystals, odorless, and having a pleasant acidulous taste, sparingly soluble in cold water and in alcohol.

Potassii et Sodii Tartras, U. S. P., $KNaC_4H_4O_6+4H_2O$.—This compound, known also as Rochelle or Seignette salt, forms large, colorless, rhombic prisms, odorless, and with a cool, saline taste. The crystals effloresce slightly in dry air. Soluble in water, almost insoluble in alcohol.

Antimonii et Potassii Tartras, U. S. P., $2K(SbO)C_4H_4O_6+H_2O$.—This compound, known also as "tartar emetic," forms colorless, transparent crystals, becoming opaque and white on exposure to the air. Soluble in water, but insoluble in alcohol. It is poisonous and acts as an emetic, and is used as a mordant in dyeing.

Ferri et Ammonii Tartras, U. S. P., and **Ferri et Potassii Tartras,** U. S. P., are uncrystallizable double salts, which are obtained as syrupy solutions and dried in films, which are then broken up, and constitute what are called "scale preparations."

The *Lævo-tartaric Acid* is like the dextro-tartaric in its chemical properties, but is the opposite in its behavior towards polarized light. When equal quantities of both acids are mixed together in aqueous solution, the solution becomes warm, and we obtain

Racemic Acid, $C_4H_6O_6+H_2O$.—Racemic acid is found sometimes in grape juice, and in the mother liquor from the crystallization of tartar. Its crystals are rhombic, efflorescent, and less soluble than those of dextro-tartaric acid. It is optically inactive. Its salts are called racemates. When the sodium-ammonium salt is crystallized from solution, the crystals obtained show hemihedral faces (*i.e.*, only one-half the faces of the normal figure are developed). Pasteur first observed that these crystals differed, part being dextro-hemihedral, and part being lævo-hemihedral, and that the lævo-hemihedral crystals were dextro-rotatory in solution, and *vice versa*. If, then, the two kinds of crystals are separated from each other mechanically, and the free acid liberated from each, it is found that we have no racemic acid remaining; but in the one case have dextro-tartaric, and in the other case lævo-tartaric acid.

If to a solution of ammonium racemate be added the ferment *Penicillium glaucum*, the dextro-tartaric acid is decompose faster than the lævo-tartaric, and the latter may thus be obtaine

Meso-tartaric Acid is also an inactive variety, but is not decon posable like racemic acid into active modifications. It is pr duced along with racemic acid in different reactions. Forms efflorescent plates, fusing at 146°.

Citric Acid, $C_3H_4(OH)(COOH)_3$ (**Acidum Citricum,** U. P.).—This important acid occurs in the free state in lemon s, oranges, etc., and, mixed with malic acid, in gooseberries, currants, and mulberries, and, as calcium salt, in wood, potatoes, beet-root, etc. Is prepared generally from lemon juice, which contains 6 to 7 per cent. of the acid. The acid is separated in the form of the difficultly soluble lime-salt; this is decomposed by sulphuric acid, and the acid solution concentrated in vacuo to the point of crystallization. A new source of citric acid manufacture has been recently announced, which may prove to be more economical than the extraction from lemon juice. Dr. Ca l Wehmer has discovered that sugar solutions exposed to the action of certain microscopic fungi, the spores of which are present in the atmosphere, become transformed into citric acid. It is claimed that 11 kilogrammes of sugar treated in this wa have yielded 6 kilogrammes of crystallized citric acid. The acid crystallizes with one molecule of water in colorless, rhombic prisms, which are odorless, and have an agreeable acid taste effloresce in warm air, and deliquesce when exposed to moist air. Is soluble in water and alcohol, slightly soluble in ether. When heated to 135° it loses its water of crystallization, melts at 153°, and breaks up at a higher temperature into aconitic acid and water, and then into itaconic acid and CO_2.

The official metallic citrates are:

Potassii Citras, U. S. P., $K_3C_6H_5O_7+H_2O$.—Forms colorless crystals or white granular powder, odorless, and with a cooling, saline taste.

Lithii Citras, U. S. P., $Li_3C_6H_5O_7$.—Forms a white powder, odorless, with a cooling, faintly alkaline taste, deliquescent on exposure to air.

Bismuthi Citras, U. S. P., $BiC_6H_5O_7$.—Forms a white amorphous or faintly crystalline powder, odorless, tasteless, and permanent in air.

Besides these crystalline salts, we have as evaporated syrups or "scale preparations:" **Bismuthi et Ammonii Ci**

U. S. P., **Ferri Citras,** U. S. P., and **Ferri et Ammonii Citras,** U. S. P. The magnesium citrate is also official in **Liquor Magnesii Citratis,** U. S. P., and **Magnesii Citras Effervescens,** U. S. P.

The monobasic pentatomic acids, *arabonic*, *xylonic*, *rhamnonic*, and *saccharinic* acids, are obtained by the oxidation of the corresponding pentose sugars. They possess only a theoretical interest.

Oxycitric Acid, $C_3H_3(OH)_2(COOH)_3$, is found in beet and turnip juice, and has been prepared artificially from aconitic acid.

The monobasic and dibasic hexatomic acids are obtainable both from the hexatomic alcohols mannite and dulcite and from the sugars related to them. The dibasic acids especially are produced from a variety of sources among the class of carbohydrates.

Saccharic Acid, $(CHOH)_4(COOH)_2$, is produced by the oxidation of cane-sugar, dextrose, mannite, or starch by nitric acid. Brittle, very hygroscopic mass, easily soluble in water. The ammonium salt of saccharic acid is decomposed at 160° into pyrrol, ammonia, and carbon dioxide : $C_6H_8(NH_4)_2O_8 = C_4H_5N + 2CO_2 + NH_3 + 4H_2O$.

Mucic Acid, $(CHOH)_4.(COOH)_2$, is obtained by the oxidation of milk-sugar, gums, and mucilages by nitric acid. White crystals, fusing at 213°, difficultly soluble in water. The ammonium salt decomposes like the corresponding salt of saccharic acid into pyrrol, carbon dioxide, and ammonia.

7. Aldehydic and Ketonic Acids.—Mention was made under the oxidation products of diatomic alcohols of alcohol acids. It is obvious that another intermediate class may be aldehyde acids, and where secondary alcohol groups exist, combined in the same molecule with primary alcoholic groups, we may obtain ketonic acids, or acids in which we have both the ketone group, CO, and the carboxyl group, COOH.

Glyoxalic Acid, CHO.COOH, is an aldehyde acid found in unripe fruits, such as grapes, gooseberries, etc. It crystallizes in prisms, easily soluble in water.

Glycuronic Acid, $COH.(CHOH)_4.COOH$, is an aldehydic acid obtained by the reduction of saccharic acid. It also possesses interest as being found in the urine as a decomposition product after taking internally such substances as camphor, phenol, phenetol, α- and β-naphthol.

Pyroracemic Acid, $CH_3.CO.COOH$ (aceto-formic acid), is a ketone acid resulting from the dry distillation of tartaric, racemic,

and glyceric acids. It is a colorless liquid, soluble in wat
hol, and ether, boiling with slight decomposition at 16
and smelling of acetic acid and extract of beef.

Aceto-Acetic Acid, $CH_3.CO.CH_2COOH$, is a stron
liquid miscible with water, and breaking up upon warm
acetone and carbon dioxide. Its ethyl ester is obtaine
form of its sodium compound by the action of sodium up
acetate, and from the ester the free acid is obtained by
cation.

Levulinic Acid, $CH_3.CO.CH_2.CH_2COOH$ (aceto-p
acid), results from the action of acids upon cane-sugar, la
cellulose, gum, starch, and other carbohydrates. A cond
product of levulinic acid with phenyl-hydrazine is k
medicine under the name of "antithermin."

VII. ESTERS, OR ETHEREAL SALTS.

These are bodies formed by the replacement of the h
of an acid, whether inorganic or organic, by an alcohol r
base. They are, as stated, ethereal salts, and may inclu
neutral, and basic salts, or esters, as more generally term

1. Esters of Inorganic Acids.—The esters of th
acids have already been described as the halogen deriva
the hydrocarbons.

The esters of nitrous acid are obtained by passing
fumes into the alcohols, or by the action of copper and ni
upon the same. They are liquids of aromatic odor, a
low boiling points, and are easily saponifiable. Nascent
gen reconverts them into alcohol, ammonia being forme
same time.

Methyl Nitrite, CH_3ONO, is gaseous at ordinary t
tures.

Ethyl Nitrite, $C_2H_5O.NO$, is a mobile liquid of pen
ethereal odor and peculiar stinging taste. Boils at 18°, a
with a bright white flame. Its alcoholic solution is the **S**
Ætheris Nitrosi, U. S. P., known also as "sweet s
nitre." This is stated by the U. S. Pharmacopœia to
alcoholic solution of ethyl nitrite yielding, when fres
pared and tested in a nitrometer, not less than 11 times
volume of nitrogen dioxide." The official spirit is 22 ti
weight of the ethyl nitrite contained. It is now made
action of sulphuric acid upon a mixture of sodium nit
alcohol.

A one-per-cent. alcoholic solution of nitroglycerin constitutes the **Spiritus Glonoini,** U. S. P.

Nitro-erythrite, $C_4H_6(NO_3)_4$, and *Nitro-mannite*, $C_6H_8(NO_3)_6$, are similar esters of nitric acid, and are like nitroglycerin in explosive characters, although less violent.

The esters of sulphuric acid are formed by the action of sulphuric acid upon the alcohols. As sulphuric acid is dibasic, two series of esters are possible, just as acid and neutral sulphates of inorganic bases are formed.

Acid Ethyl Sulphate (or Ethyl-sulphuric Acid), $C_2H_5HSO_4$, is obtained on mixing equal parts of absolute alcohol and concentrated sulphuric acid. The free acid is a syrup easily soluble in water. Under the old name of "sulpho-vinic acid," it has long been known as the intermediate product in the "continuous ether process" (see p. 585). Its salts, formerly called "sulphovinates," crystallize well. They are, of course, double sulphates of ethyl and metallic base.

Neutral Ethyl Sulphate, $(C_2H_5)_2SO_4$, is a colorless, oily liquid, insoluble in water, of a pleasant peppermint odor. It boils at 208°. The corresponding esters of sulphurous acid are known, but are prepared with more difficulty, as the isomeric sulphonic acid derivatives (see p. 588) tend to form by the reaction with metallic sulphites.

The esters of phosphoric, silicic, and carbonic acids are also known. The last of these will be referred to later. (See Carbonyl Derivatives.)

2. **Esters of Organic Acids.**—These form in some cases by the direct action of the acids upon the alcohols, but more generally it is necessary to provide for taking up the water which forms in the reaction. This is done by the addition of sulphuric acid as dehydrating agent to the mixture of alcohol and organic acid, or still more readily by passing dry HCl gas into a mixture of the alcohol and acid. This probably acts by first forming an acid chloride with the radical of the organic acid, and this then reacts with the alcohol.

The esters of the lower members of the fatty acid series are for the most part colorless, neutral liquids, which volatilize without decomposition. As a rule they are insoluble in water, but soluble in alcohol and ether. The esters of the higher acids are solids, and play an important part in nature as the natural fats and waxes.

The esters are, without exception, saponifiable; that is, under the influence of water or alkalies and acids they break up into the free alcohol and acid, or alkaline salt of the acid, in case alkalies are used for the saponification.

Æthyl Formate, $HCO.OC_2H_5$.—Boils at 55°. Is employed in the manufacture of artificial rum or arrack, as well as in peach essence and other fruit essences.

Æthyl Acetate, $C_2H_3O.OC_2H_5$ (**Æther Aceticus**, U. S. P.). Boils at 77.5°; is a transparent, colorless liquid of fragrant and refreshing odor and a peculiar acetous and burning taste; is moderately soluble in water, easily soluble in all proportions in alcohol, ether, fixed and volatile oils. It is inflammable, burning with a yellowish flame and acetous odor. Besides being used internally in medicine, it is largely used in admixture in fruit essences and as a solvent.

Amyl Acetate, $C_2H_3O.OC_5H_{11}$.—Boiling point 148°. This ester has a characteristic fragrant odor of pears, and hence is the basis of the artificial pear essence. It is also used largely as an ingredient in the manufacture of pyroxylic varnishes, owing to its solvent power.

Octyl Acetate, $C_2H_3O.OC_8H_{17}$.—Boiling point 210°. Forms the chief constituent of the oil from the fruit of *Heracleum spondylium*.

Æthyl Butyrate, $C_4H_7O.OC_2H_5$.—Boiling point 120.9°; possesses the characteristic odor of pineapples, and hence is used in that fruit essence.

Iso-amyl Butyrate, $C_4H_7O.OC_5H_{11}$.—Boiling point 178.6°. Is also used in the manufacture of pineapple essence.

Æthyl Iso-valerate, $C_5H_9O.OC_2H_5$.—Boiling point 134.3°. Is a constituent of melon and peach oils.

Iso-amyl Iso-valerate, $C_5H_9O.OC_5H_{11}$.—Boiling point 196°. Is the chief constituent of apple essence.

Iso-amyl Caprinate, $C_{10}H_{19}O.OC_5H_{11}$.—Boiling point 275°, with partial decomposition. This is the chief constituent of wine fusel oil, and under the misapplied name of "œnanthic ether," gives the bouquet to wine.

Cetyl Palmitate, $C_{16}H_{31}O.OC_{16}H_{33}$.—Fusing point 53.5°. This ester forms the chief constituent of spermaceti (**Cetaceum**, U. S. P.), a peculiar, fatty solid obtained from the head of the sperm whale (*Physeter macrocephalus*). This solid ester is held dissolved in the sperm oil during the life of the animal, and after death, with the disappearance of the animal heat, it crystallizes out. It forms a white, somewhat translucent, slightly unctuous mass, of a scaly, crystalline fracture and pearly lustre; odor[illegible] and with a bland, mild taste. Sp. gr. about 0.945 at 15°. It is insoluble in water, and nearly so in cold alcohol; soluble in boiling alcohol, also in ether, chloroform, carbon disulphide, fixed and volatile oils.

Ceryl Palmitate, $C_{16}H_{31}O.OC_{27}H_{55}$.—Fusing point 79°. Is the chief constituent of opium wax.

Myricyl Palmitate, $C_{16}H_{31}O.OC_{30}H_{61}$.—Fusing point 72°. Is the part of beeswax insoluble in alcohol, the soluble part consisting largely of cerotic acid (see p. 601). Beeswax (**Cera Flava**, U. S. P.) is an animal product, being the material of the cell walls of the combs of the *Apis mellifica*, or honey bee. It is a yellowish to brownish-yellow solid, having an agreeable, honey-like odor, and a faint, balsamic taste. Sp. gr. 0.955 to 0.967 at 15°; melting point 63°–64°. It is insoluble in water, sparingly soluble in cold alcohol, but almost completely soluble in boiling alcohol. It is completely soluble in ether, chloroform, and fixed and volatile oils.

Beeswax is bleached white to adapt it for use in candle-making and other purposes. This is accomplished either by the action of light and air (air-bleached wax), or by the use of oxidizing agents, such as potassium dichromate, potassium permanganate, and hydrogen dioxide (chemically-bleached wax). The product is a yellowish-white solid (**Cera Alba,** U. S. P.), which is slightly more crystalline than the yellow wax, and contains rather more free acid.

Ceryl Cerotate, $C_{27}H_{53}O.OC_{27}H_{55}$.—Fusing point 82°. Forms the chief ingredient of Chinese insect wax. It is also found in opium wax.

Myricyl Cerotate, $C_{27}H_{53}O.OC_{30}H_{61}$, is found in carnauba wax.

Probably the most important of the esters of organic acids, however, are the compounds of the triatomic alcohol glycerin. The esters of this alcohol with the members of the fatty acid series make up the bulk of the vegetable and animal fats and fatty oils. While glycerin as a triacid base can form esters containing one, two, or three molecules of fatty acid, we find that the naturally occurring compounds are exclusively neutral esters,—that is, contain three molecules of the monobasic acid in combination with the base. The mono-acid and di-acid compounds can be formed artificially, however, in many cases.

The most important of the glycerin esters are:

Monoformin, $C_3H_5(OH)_2OCHO$, and *Diformin*, $C_3H_5(OH)(OCHO)_2$, have been obtained artificially; the former by heating

Tristearin, $C_3H_5(OC_{18}H_{35}O)_3$, occurs in most of the solid fats and in a large number of the liquid fats associated with palmitin and olein. It is difficult to obtain the tristearin perfectly free from tripalmitin, even after repeated crystallizations, but it has been claimed that it can be obtained perfectly free from the seeds of *Brindonia indica*. Fuses at first at 55°, but after repeated melting shows a permanent melting point of 71.5°.

Both *Monostearin*, $C_3H_5(OH)_2(OC_{18}H_{35}O)$, and *Distearin*, $C_3H_5(OH)(OC_{18}H_{35}O)_2$, have been obtained synthetically; the former direct from glycerin and stearic acid, and the latter by the aid of the former.

Triarachin, $C_3H_5(OC_{20}H_{41}O)_3$.—This glyceride is found in earth-nut oil as well as in cocoanut oil, and the fat from the seeds of *Nephelium lappaceum*.

Tribenin, $C_3H_5(OC_{22}H_{43}O)_3$.—A glyceride found with olein in oil of ben from *Moringa oleifera*.

Trihypogæin, $C_3H_5(OC_{16}H_{29}O)_3$. —This glyceride occurs along with triarachin and triolein in earth-nut oil.

Triolein, $C_3H_5(OC_{18}H_{33}O)_3$, occurs abundantly in nature in the non-drying fatty oils, as olive and almond oils. May be obtained approximately pure by agitating olive or almond oil with a cold concentrated aqueous solution of caustic soda, which saponifies the palmitin and leaves the most of the olein unchanged. Is liquid at ordinary temperatures, but solidifies below 0°, and can be distilled in a vacuum. Only slightly soluble in alcohol, easily soluble in ether. By treatment with nitrous acid it is converted into solid white elaïdin, a polymeric compound.

Tridoeglin, $C_3H_5(OC_{19}H_{35}O)_3$.—The glyceride of doeglic acid forms the chief constituent of the oil of the doegling, or bottle-nose whale.

Trierucin, $C_3H_5(OC_{22}H_{41}O)_3$.—This glyceride occurs in the oil of the white and the black mustard-seed, in rape oil and grape-seed oil. Nitrous acid converts it into the isomeric *tribrassidin*.

Trilinolein, $C_3H_5(OC_{18}H_{31}O)_3$.—This glyceride is the characteristic constituent of the drying oils, such as linseed oil, poppy-seed oil, sunflower oil, and hempseed oil. It does not yield a solid product with nitrous acid, but is characterized by the readiness with which it absorbs oxygen and thickens with the formation of resinous products.

Triricinolein, $C_3H_5(OC_{18}H_{33}O_2)_3$.—This glyceride is the peculiar constituent of castor oil. It forms a solid polymeric product known as ricinelaidin when treated with nitrous acid.

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ifferences, is that of A. H. [illegible]

(*a*) *Olive Oil Group.*—[illegible]
g oils. Lighter than groups [illegible]
ith nitrous acid. Includes [illegible]
ed, and mustard oils.

(*b*) *Cotton-seed Oil Group.*—Intermediate [illegible]
on-drying oils. Undergo more or less [illegible]
ield little or no elaidin. Includes [illegible]
ower, hazel-nut, and beech-nut oil.

(*c*) *Linseed Oil Group.*—Vegetable drying [illegible]
laidin. Of less viscosity than the non-drying oils. Includes
inseed, hemp-seed, poppy-seed, niger-seed, and walnut [illegible]

(*d*) *Castor Oil Group.*—Medicinal oils. Very viscous and of high density. Includes castor and croton oils.

(*e*) *Palm Oil Group.*—Solid vegetable fats. Do not contain notable quantities of the lower fatty acids. Includes palm oil, cacao butter, nutmeg butter, and shea butter.

(*f*) *Cocoanut Oil Group.*—Solid vegetable fats, in part wax-like. Several contain notable proportions of the glycerides of lower fatty acids. Includes cocoanut oil, palm-nut oil, laurel oil, Japan wax, and myrtle wax.

(*g*) *Lard Oil Group.*—Animal oleins. Do not dry notably on exposure, and give solid elaidins with nitrous acid. Includes neat's-foot oil, bone oil, lard oil, and tallow oil.

(*h*) *Tallow Group.*—Solid animal fats, predominantly glycerides of palmitic and stearic acids, although butter contains lower glycerides. Includes tallow, lard, bone fat, wool fat, butter fat, oleomargarine, and manufactured stearin.

(*i*) *Whale Oil Group.*—Marine animal oils. Characterized by offensive odor and reddish-brown color when treated with caustic soda. Includes whale, porpoise, seal, menhaden, cod-liver, and shark-liver oils.

(*j*) *Sperm Oil Group.*—Liquid waxes. Are not glycerides, but esters of monatomic alcohols. Yield solid elaidins. Includes sperm oil, bottle-nose or doegling oil, and dolphin oil.

(*k*) *Spermaceti Group.*—Waxes proper. Are compound ethers or esters of higher monatomic alcohols, with higher fatty acids in the free state. Includes spermaceti, beeswax, Chinese wax, and carnauba wax.

The composition of the natural fats as essentially compounds of the fatty acids with glycerin was first definitely ascertained by Chevreul in 1823, and with this knowledge was also indicated the means of decomposing them. Chevreul first used alkalies for that purpose, and that method is still applied if the alkaline salts of the fatty acids (soaps) are desired. For the purpose of obtaining the fatty acids as such, or the glycerin, other methods have been adopted.

We may summarize the several methods employed for this decomposition under three headings, although practically there are additional methods of decomposition in use which involve a combination of several of these general reactions.

1st. The decomposition of the fats by the action of alkalies. This original method of Chevreul is only employed when the manufacture of a soap is the end desired. We may illustrate it by the example of the reaction between palmitin and an alkali such as would take place in the manufacture of a palm-oil soap.

$$\underset{\text{Tripalmitin.}}{C_3H_5\left\{\begin{matrix}OC_{16}H_{31}O\\ OC_{16}H_{31}O\\ OC_{16}H_{31}O\end{matrix}\right.} + 3HONa = \underset{\text{Glycerin.}}{C_3H_5\left\{\begin{matrix}OH\\ OH\\ OH\end{matrix}\right.} + \underset{\text{Sodium Palmitate.}}{3C_{16}H_{31}OONa.}$$

2d. The decomposition of the fats by the action of metallic oxides in the presence of water. Chevreul's use of alkalies was replaced already in 1831 by that of lime, suggested by De Milly, and the use of lime and water under pressure constitutes the "autoclave" process of to-day. This will be referred to and illustrated later in a short section on the "Industries of the Fats." Pharmacists make use of a reaction of this kind in the manufacture of lead plaster (**Emplastrum Plumbi**, U. S. P.), in which the olein of olive oil is decomposed by litharge in the presence of water:

$$\underset{\text{Triolein.}}{2C_3H_5\left\{\begin{matrix}OC_{18}H_{33}O\\ OC_{18}H_{33}O\\ OC_{18}H_{33}O\end{matrix}\right.} + 3PbO + 3HOH = \underset{\text{Glycerin.}}{2C_3H_5\left\{\begin{matrix}OH\\ OH\\ OH\end{matrix}\right.} +$$

$$\underset{\text{Lead Oleate.}}{3Pb(OC_{18}H_{33}O)_2.}$$

3d. The decomposition of the fats by the action of steam or water under pressure. The discovery of the possibility of effecting the "saponification" of the fats by water alone, made in 1854 by Tilghman, has since been utilized very extensively under various forms of procedure. The reaction may be illustrated by the decomposition of stearin:

$$\underset{\text{Stearin.}}{C_3H_5\left\{\begin{matrix}OC_{18}H_{35}O\\ OC_{18}H_{35}O\\ OC_{18}H_{35}O\end{matrix}\right.} + 3HOH = \underset{\text{Glycerin.}}{C_3H_5\left\{\begin{matrix}OH\\ OH\\ OH\end{matrix}\right.} + \underset{\text{Stearic Acid.}}{3C_{18}H_{36}O_2.}$$

The decomposition by sulphuric acid with after-distillation of the fatty acids is nothing more than a saponification by water in the presence of the acid, although with certain classes of fats it has advantages in increasing the yield of solid fat acids.

INDUSTRIES OF THE FATS.

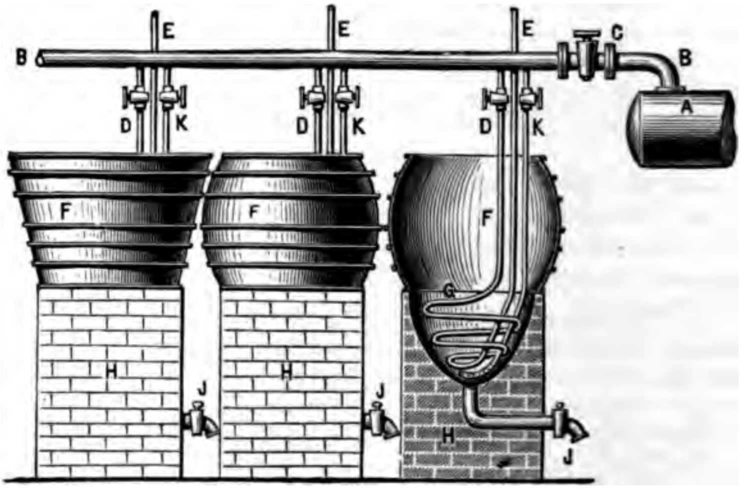
The great importance of many of the vegetable and animal fats as raw materials of large industries justifies us in noticing these industries in outline, and giving a short account of the practical side of them.

1. **Soap-making.**—Soaps are most generally made by the direct saponification of the fat with alkali, although where the fatty acids have been obtained in the free state and then worked, as described later, for the extraction of the solid acids for candle-making, the oleic acid, or "red

oil," remaining over is also utilized for soap-making. Soaps are made chiefly from tallow, cotton-seed oil, cocoanut oil, palm oil, and olive oil. We may divide the soaps, first, into the *hard soaps*, in which the base is soda or a mixture of soda and potash, and *soft soaps*, in which the base is potash. In the manufacture of this latter class the drying oils are preferably used, as in the official **Sapo Mollis**, U. S. P.

True hard soaps are manufactured by boiling the fats in open vessels, with the aid of steam heat, with alkaline lyes of gradually increasing strength, until products of definite character are obtained. The "soap-copper," as shown in Fig. 94, is an iron kettle, or series of kettles, set in masonry and equipped with pipes for both open and closed steam, and provided with an outlet for the discharge of the waste lyes when required. Strong lyes are not used at first or saponification will not take place. A soda-lye of about 11° B., equal to one-fourth that needed for complete saponification, is first run in with the melted fat. When this mixture becomes homogeneous, lye of 20° to 25° B., equal in amount to that taken before, is cautiously added, and boiling is kept up until a sample taken out has a firm consistence between the fingers. It is then salted with a brine of 24° B., and the contents of the copper allowed to stand for several hours at rest. Two layers will then have formed, an upper layer of soap-paste containing water, and a lower one, of "spent-lye," containing the salt and the glycerin in solution. After removing this spent-lye from below, the rest of the caustic soda for saponification is run in and the soap boiled up again.

FIG. 94.



Soap-coppers.

If a "rosin soap" is desired the rosin is added at this stage, otherwise a "curd soap" is the product. The boiling is now continued until the frothing subsides and the mixture boils clear. The contents of the copper are then boiled with open steam, and a small quantity of lye of 12° B. is run in until the soap separates in flakes and feels hard when cold. Boiling is usually continued for several hours to insure complete saponification, and it is then allowed to separate and harden. If it is transferred to the cooling-frames before this hardening and separation is completed, a mottled soap may be obtained. A solution of ferrous sulphate added at this point produces a peculiar greenish mottled appearance, becoming red on exposure to the air, characteristic of Marseilles and Castile soaps. In smooth or "cut soaps" water or thin lye is added to the contents of the copper before the soap separates finally to form the curd, and is taken up, giving a smooth yet firm surface to the soap instead of the hard granular appearance of the true curd soap.

In the "cold process" soaps, exact weights of well-refined fats and the necessary caustic soda are used and added together at once. After short standing, they are agitated in a revolving copper provided with paddles at a temperature of not over 120° F. The materials rapidly coalesce, although the reaction is only finished after some days' standing in the cooling-frames. It is obvious that in this case all the glycerin of the fats originally taken remains distributed throughout the soap. Filling and padding materials can also be added in this case, and will be held in the soap. A small quantity of cocoanut oil added to the tallow or other fat facilitates the working of this cold process.

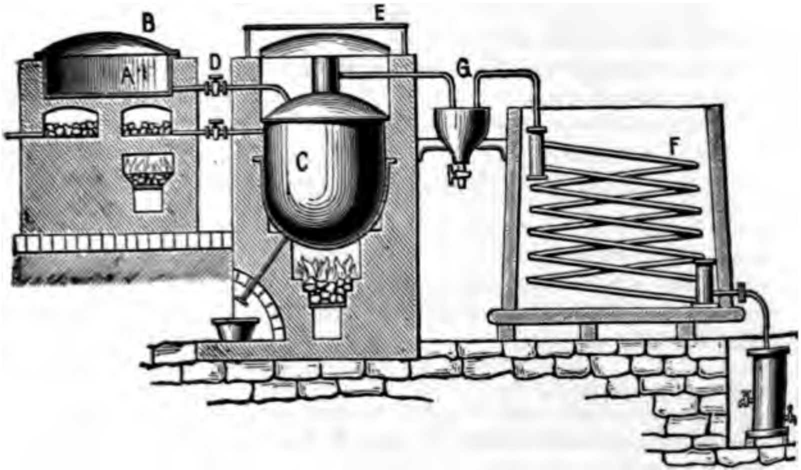
When "red oil" or oleic acid from the stearic acid candle manufacture is used, it may be saponified either with alkali or with alkaline carbonate, although the former is preferred. The oleic acid may also be changed first into the isomeric elaidic acid by the action of nitrous acid, and a very fine soap is then obtained resembling a tallow soap.

Compact soaps may contain from 10 to 25 per cent. of water, smooth or cut soaps may contain from 25 to 45 per cent., and filled soaps from 45 to 72 per cent. of water, besides the glycerin and impurities.

2. **Stearic Acid Candle Manufacture.**—Where the solid fatty acids are desired for the manufacture of candles, the fats are saponified either by the "autoclave process" of Milly, in which lime and hot water, under a pressure of 8 to 10 atmospheres, are made to decompose the fats, or they are decomposed with superheated steam, either with or without the addiion of sulphuric acid. In the former process the lime forms a lime soap, vhich is afterwards decomposed by sulphuric acid, and the free fat acids re thoroughly washed by the aid of steam. The amount of lime taken not sufficient to completely neutralize the fatty acids, as the steam demposes the lime soap first formed and allows the base to attack fresh antities of the fat. In the second process, that of superheated steam, e products are obtained quite pure and free from all foreign matters. s carried out in the Wilson and Gwynne form of apparatus, it is shown Fig. 95. The fat is first heated in A by waste heat from the superater below, and then flows into the retort C, which must be kept at m 290° to 315° C., and for this purpose is covered in. The superheated am at 315° C. comes into the retort by the side tube, after some 24 to hours the contents of the retort are distilled off, the fatty acids con-

densing first, and the watery glycerin passing on to the farther condensing vessel. In this way a very pure commercial glycerin is obtained as well as pure fatty acids. If the temperature much exceed 315° C., acrolein forms from the decomposition of the glycerin. For the extraction of the hard stearic acid the washed fatty acids are now melted and run into troughs or dishes of tin, as shown in Fig. 96. These are placed in a room at a temperature of 20° to 30° C. and kept for two or three days, to allow the palmitic and stearic acids to crystallize, when the contents are emptied into canvas or woollen bags and pressed in an hydraulic press. The liquid oleic acid runs off, and the cakes of crude stearic acid obtained are melted and again put to crystallize at a somewhat higher temperature than before. A thorough pressing will now leave the stearic acid sufficiently firm for candle-making. A little wax or paraffin is usually added to take away the very crystalline structure, which unfits stearic acid somewhat for candle-making.

Fig. 95.



Decomposition of the fats.

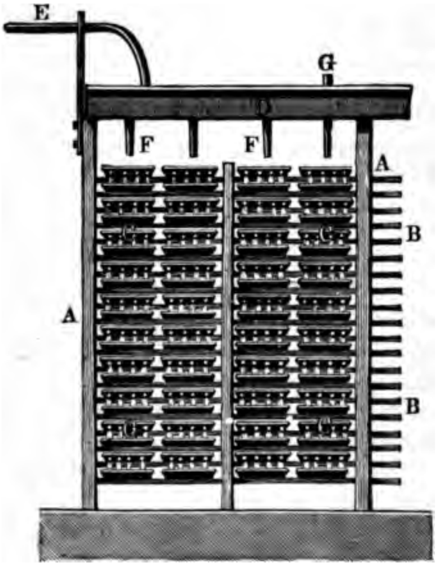
3. **Oleomargarine, or Artificial Butter.**—When very pure fats are taken and care is exercised in the melting and rendering, it is possible to separate solid stearin by a chilling process similar to that just described for stearic acid, and obtain as a liquid product the mixture of olein and palmitin known popularly as "oleomargarine oil." This so-called "oleo oil" is then churned with about 10 per cent. of its weight of milk, with the addition of a little butter color, and the product is salted and brought into the market as oleomargarine butter. In making what is called "butterine," neutral lard is added to the oleo oil and milk before churning, and then finished as before. At times a small quantity of sesame oil or cotton-seed oil is added to soften the texture of the product.

4. **Manufacture of Glycerin and Nitroglycerin.**—Glycerin is obtained in connection with the saponification of fats by the autoclave process with

me or the saponification with superheated steam. The glycerin from e lime process is obtained in a very dilute state at first, and must be ncentrated. This is done by the aid of steam, at first with free access air, and later in vacuo. The product, brought to a specific gravity of 22, has a brown color and is known as "raw glycerin." It is then tered through bone-black in closed and jacketed filters, and distilled ith the aid of steam. The glycerin which distils over from the saponiation in the apparatus of Wilson and Gwynne, before described, is ore concentrated and freer from impurities. It still requires, however, e concentration and after-distillation with steam heat.

Nitroglycerin is a technical product of great commercial importance, ecause of its large use in ining and blasting operaons. It is manufactured a large scale, but every age of the process must be atched with the greatest re because of the extreme anger connected with its xplosions. The nitrating ixture consists of 5 parts concentrated sulphuric cid and 3 parts of nitric cid of 1.48 sp. gr. The lycerin must be relatively ure, and of sp. gr. about .26. The acid mixture aving been placed in a ooden tank lined with ad, and cooled, by coils of aden pipe through which e water is circulating, to ° to 16° C., the glycerin is in in through a small pipe, r, better, in a fine spray rough a metal sieve. The quid must be kept continuously mixed during the nitration, and the mperature not allowed to rise above about 18°. If the temperature rise uddenly or continue rising, the contents of the tank must be allowed to un at once into a larger receptacle containing cold water. The nitration f 730 pounds of glycerin takes from ½ to 2½ hours. When it is comleted the product is run into a vessel containing water at 21°. As the itroglycerin separates, it is then washed first with pure water, then with ater containing some soda solution, and finally with strong soda soluon. The yield of nitroglycerin is greater in winter than in summer, arying from 950 to 1200 pounds of nitroglycerin from 630 pounds of lycerin. The several operations of nitration, separation, and washing re all carried out in detached buildings, and, as far as possible, comressed air is used for effecting the mixing and washing.

Fig. 96.



Granulation of stearic acid.

5. The Utilization of the Drying Oils in Paints and Varnishes.—In the classification of the oils (see p. 621) the distinction was made between drying and non-drying oils. This distinction is based upon differences in chemical composition. The drying oils, like linseed oil, contain large amounts of the glyceride of linoleic acid, which differs from oleic acid chiefly in its power of absorbing oxygen and becoming resinous. This tendency is notably accelerated by boiling the oils with certain mineral compounds like litharge, manganese dioxide, and the acetates and borates of lead, manganese, and zinc. These are known therefore as "dryers" because of the drying quality they impart to the oils. This is of great importance in the manufacture of paints and varnishes. In a paint we have the finely divided color thoroughly rubbed up and incorporated with boiled linseed oil, and this is then thinned out with oil of turpentine. In varnishes we have solutions of hard resins in oil, also thinned out, if necessary, with oil of turpentine. The resins so used are amber, copal, damar, animé, etc.

Printers' ink is also a thoroughly boiled linseed oil varnish with which is incorporated the lamp-black or other color and a small quantity of soap. Oilcloth and linoleum are also products into which boiled linseed oil enters.

VIII. AMINES AND AMIDES.

The introduction of an alcohol or basic radical into the ammonia molecule replacing one or more hydrogen atoms gives us an *amine*, and just as ammonia can combine with a haloid acid to form an ammonium salt, so the amine or derived ammonia can unite with the chloride, bromide, or iodide of an alcohol radical to form a derived ammonium salt in which, for instance, the four hydrogen atoms of NH_4Cl may be replaced by alcohol radicals.

We may have ***primary***, ***secondary***, or ***tertiary*** amines, according as one, two, or three atoms of hydrogen in NH_3 are replaced. We may also have monamines, diamines, or triamines, according as one, two, or three molecules of ammonia are represented. Thus:

$NH_2.CH_3$, methylamine, is a primary amine.

$NH.(CH_3)_2$, dimethylamine, is a secondary amine.

$N(CH_3)_3$, trimethylamine, is a tertiary amine.

$(NH_2)_2.C_2H_4$, ethylenediamine, is a diamine.

$N(C_2H_5)_4.OH$, tetraethyl ammonium hydrate, is a quaternary base.

$N(CH_3)_4I$, tetramethyl ammonium iodide, is a quaternary salt.

The amines containing the lower alcohol radicals bear a close resemblance to ammonia, being strongly basic, having an ammoniacal odor, forming white clouds with hydrochloric acid, forming salts with haloid acids, which salts unite to form crystalline double strongly ammoniacal smell and biting taste. It differs from ammonia in dissolving $Al_2(OH)_6$, but does not dissolve $Fe_2(OH)_6$.

Diethylamine, $(C_2H_5)_2NH$, boils at 56°. Does not dissolve Zn OH)$_2$.

Triethylamine, $(C_2H_5)_3N$, is an oily, strongly alkaline liquid, boiling at 90°. It is found in the decomposition of fish tissue.

Trimethyl-vinyl Ammonium Hydrate (Neurin), $N(CH_3)_3C_2H_3$-OH.—This base, containing the unsaturated radical vinyl, results when lecithin and protagon, which are found in nerve and brain tissue, are boiled with baryta. Very soluble in water, and of alkaline reaction. Extremely poisonous.

Trimethyl-oxyethyl Ammoninm Hydrate (Choline or Bilineurin), $N(CH_3)_3(C_2H_4OH).OH$, is found in the bile (χολή, bile), brain, yolk of egg, etc., being combined with glycerin-phosphoric acid as *lecithin*. It is also present in herring brine, hops, beer, and in many fungi. Choline is a strong base, difficultly crystallizable, and deliquescent. It is not poisonous.

2. **Diamines.**—*Ethylene-diamine*, $C_2H_4(NH_2)_2$, is a colorless liquid, boiling at 116.5°, easily soluble in water, not miscible with benzene and ether. It smells faintly ammoniacal, and has a caustic taste.

Diethylene-diamine, $(C_2H_4)_2(NH)_2$.—This base, known also as "Piperazin," is formed by the heating of the ethylene-diamine hydrochlorate. Rhombic tablets, fusing at 104° and boiling at 145°. Used considerably in medicine because of its solvent action on uric acid and gouty concretions.

Trimethylene-diamine, $C_3H_6(NH_2)_2$.—Oily liquid, boiling at 136°.

Tetramethylene-diamine, $C_4H_8(NH_2)_2$.—This base, known also as "Putrescin," results from the decomposition of flesh, hence contained in the cadaver. The free base smells like spermatic fluid, boils at 156°–157°, and is poisonous. It is also found in the urine and fæces in cystinuria.

Pentamethylene-diamine, $C_5H_{10}(NH_2)_2$.—This base is known as "Cadaverine." It is formed in the decomposition of flesh and fish, and, as the name indicates, is found in the cadaver. The free base boils at 178°–179°, and smells like spermatic fluid. Is poisonous. The chlorhydrate when heated breaks up into piperidine, $C_5H_{11}N$, and ammonium chloride.

The amides and imides are derivatives of ammonia, in which one or more hydrogen atoms are replaced by acid radicals. They are easily distinguished from the amines by their ready saponification. They decompose on heating with acids or alkalies, or even with water, into their components, acid and ammonia. They may be formed by the action of ammonia upon the chlorides of the acid radicals, by the dry distillation of the ammonia salts of the fatty acids, and other methods.

Formamide, $HCO.NH_2$, is obtained by heating ammonium formate to 230°. Liquid boiling at 195° with partial decomposition into NH_3 and CO. Its compound with chloral has already been noted (see Chloralamide, p. 592). It dissolves mercuric oxide, forming, with elimination of water, a compound "mercury-formamidate," $\begin{matrix}HCO.NH\\HCO.NH\end{matrix}{>}Hg$, which is used somewhat in medicine. The compound is stable in the presence of albuminoids, but is decomposed by dilute acids or alkalies, with separation of fine gray metallic mercury.

Acetamide, $C_2H_3O.NH_2$.—Obtained by heating ammonium acetate to 230°. Forms crystals easily soluble in water and alcohol, fusing at 82°, and boiling at 222°. Has a characteristic odor, recalling mice.

Diacetamide, $(C_2H_3O)_2NH$, forms a white mass, fusing at 78° and boiling at 223°.

Triacetamide, $(C_2H_3O)_3N$.—White needles, melting at 79°; neutral reaction.

The amido acids have been noted in part as derivatives under the several fatty acids (see p. 604). Some additional compounds of this class remain to be noted.

Amido-succinic Acid (Aspartic Acid), $COOH.CH_2.CH(NH_2).COOH$, is readily obtained by boiling asparagin with acids or alkalies. Formed also in the decomposition of albuminoids, horn, and glue, with acids or alkalies. It forms small rhombic tablets easily soluble in hot water. Nitrous acid changes it into malic acid.

Amido-succinamide (Asparagine), $COOH.CH_2.CH(NH_2.CONH_2$, occurs very widely distributed in the vegetable kingdom, as in sugar-beets, potatoes, in the shoots of many vegetables, in sweet almonds and asparagus, whence the name. Forms lustrous rhombic crystals, easily soluble in hot water, insoluble in alcohol and ether. Is a monobasic acid, which combines with bases, acids, and salts. It forms a crystalline blue copper salt, which is nearly insoluble in water.

Amido-pyrotartaric Acid (Glutamic Acid), $COOH.C_3H_5(NH_2).COOH$, occurs along with aspartic acid in all the decompositions of albuminoids, etc. Forms rhombic crystals, melting at 202°, soluble in water, difficultly soluble in alcohol.

Amido-pyrotartaramide (Glutamine), $COOH.C_3H_5(NH_2).CONH_2$, accompanies asparagin in many plants, and is best obtained from the fresh juice of the sugar-beet.

Appendix to Amines and Amides.—Analogous to the organic ammonia derivatives are the corresponding compounds derived from ***phosphine*** PH_3, from *arsine*, AsH_3, and *stibine*, SbH_3. Ethyl phosphine and triethyl phosphine are both liquids of powerful and disagreeable odor, which readily ignite, and burn in the air like the spontaneously inflammable phosphine. Tetraethyl-phosphonium iodide is also known. The organic arsenic compounds are primary, secondary, and tertiary arsines. Of these the best known are the secondary compounds. When an acetate like $KC_2H_3O_2$ is distilled with arsenous oxide, As_2O_3, there is produced a compound, $\begin{array}{l}As(CH_3)_2\\ |\\ As(CH_3)_2\end{array}$, known as *cacodyl* (from κακώδης, stinking), together with the oxide of the same, $\begin{array}{l}(CH_3)_2As\\ (CH_3)_2As\end{array}\!\!>O$, known as cacodyl oxide. The crude mixed distillate was first obtained by Cadet, in 1760, and called "alkarsin," and investigated by Bunsen in 1838. The free base cacodyl is of sickening odor, inciting to immediate vomiting.

The antimony, boron, and silicon compounds have also been obtained, the last named derived from SiH_4, resembling the methane derivatives.

Organo-metallic compounds, such as zinc-methyl, $Zn(CH_3)_2$, and zinc-ethyl, $Zn(C_2H_5)_2$; mercury-methyl, $Hg(CH_3)_2$, and mercury-ethyl, $Hg(C_2H_5)_2$; aluminum-methyl, $Al(CH_3)_3$; lead-methyl, $Pb(CH_3)_2$, and lead-ethyl, $Pb(C_2H_5)_2$; and tin-tetramethyl, $Sn(CH_3)_4$, and tin-tetraethyl, $Sn(C_2H_5)_4$, have all been prepared.

IX. CARBOHYDRATES.

We find very widely distributed in the vegetable kingdom a class of compounds which are of the greatest importance as food-products in the support of animal life, and play an important part in the nutrition of the living organism. These compounds have been termed "carbohydrates," because they contain along with carbon the elements hydrogen and oxygen in the ratio of 2 to 1 or as they exist in water. They also bear a simple relation to the hexatomic alcohols mannite and dulcite (see p. 582), the formula of which were $C_6H_{14}O_6$. As the formula of one group of carbo-hydrates is $C_6H_{12}O_6$, and several of them can be formed by the careful oxidation of these hexatomic alcohols, it was suppos they were aldehydes or ketones of these alcohols, and such fact they proved to be. A second group of the carbohydrat with the formula $C_{12}H_{22}O_{11}$, seem to be simply anhydrides of first aldehydic or ketonic group; and the third group, with the formula $(C_6H_{10}O_5)_n$, are still more complex anhydrides. The process of "hydrolysis" is capable of causing these anhydrides to take up water and yield compounds of the other group. Despite the large number of these carbohydrates occurring in nature, until very recently it had not been found possible to form any of them by synthetic means. A beginning has now been made in this work, however, by the German chemist Emil Fischer, and, while the more important of the carbohydrates still remain incapable of artificial formation, the way is clearly indicated. The number of artificial compounds formed makes it necessary to broaden the classification hitherto adopted, and, instead of the old grouping of *Glucoses*, $C_6H_{12}O_6$, *Sucroses*, $C_{12}H_{22}O_{11}$, and *Amyloses*, $(C_6H_{10}O_5)_n$, we now classify them as follows:

I. Monosaccharides.—

Trioses.—Glycerose, $C_3H_6O_3$ (prepared from glycerin by oxidation).

Tetroses.—Erythrose, $C_4H_8O_4$ (prepared from erythrite by oxidation).

Pentoses.—Arabinose, $C_5H_{10}O_5$ (prepared by the action of dilute sulphuric acid upon lævo-rotatory gum arabic); xylose, $C_5H_{10}O_5$ (prepared by boiling beech-wood and jute with dilute acids); ribose, $C_5H_{10}O_5$ (prepared from arabinose by heating with pyridine); rhamnose or isodulcite, $C_5H_9(CH_3)O_5$, a methyl-pentose (prepared by the decomposition of glucosides like quercitrin); fucose, $C_5H_9(CH_3)O_5$ (obtained from sea-weeds by hydrolysis).

Hexoses are divided into two groups,—the *aldoses*, in which the aldehydic character is shown, and the *ketoses*, in which the ketone character is indicated by their reactions. To the aldose group belong mannose, $C_6H_{12}O_6$ (obtained by the careful oxidation of mannite); glucose, $C_6H_{12}O_6$ (of which the dextro-rotatory variety is the naturally occurring dextrose); gulose, $C_6H_{12}O_6$ (obtained as yet only artificially); galactose, $C_6H_{12}O_6$ (obtained by the inversion of milk sugar); talose, $C_6H_{12}O_6$ (obtained as yet only artificially); rhamno-hexose, $C_6H_{11}(CH_3)O_6$ (obtained artificially from rhamnose). To the ketose group belong fructose (or levulose), $C_6H_{12}O_6$ (obtained along with glucose in the inversion of cane-sugar); acrose, $C_6H_{12}O_6$ (obtained as yet only artificially); sorbinose, $C_6H_{12}O_6$ (obtained from mountain-ash berries).

Heptoses.—Manno-heptose, $C_7H_{14}O_7$ (obtained artificially from mannose); gluco-heptose, $C_7H_{14}O_7$ (obtained artificially from glucose).

Octoses.—Manno-octose, $C_8H_{16}O_8$ (obtained artificially from mannose); gluco-octose, $C_8H_{16}O_8$ (prepared from the corresponding glucose).

Nonoses.—Manno-nonose, $C_9H_{18}O_9$ (prepared from the corresponding mannose); gluco-nonose, $C_9H_{18}O_9$ (prepared from the corresponding glucose).

2. Disaccharides and Trisaccharides.—

Tribioses and *Tetrabioses* are as yet unknown.

Pentabioses.—Arabinon, $C_{10}H_{18}O_9$ (has been prepared by the moderated action of dilute sulphuric acid upon arabic acid).

Hexabioses.—Sucrose (cane sugar), $C_{12}H_{22}O_{11}$; lactose (milk sugar), $C_{12}H_{22}O_{11} + H_2O$; maltose, $C_{12}H_{22}O_{11}$; isomaltose, $C_{12}H_{22}O_{11}$; trehalose (mycose), $C_{12}H_{22}O_{11}$; melabiose (eucalyn), $C_{12}H_{22}O_{11}$; turanose, $C_{12}H_{22}O_{11}$ (obtained by the partial hydrolysis of melezitose).

Hexatrioses.—Meletriose (raffinose), $C_{18}H_{32}O_{16}$; melezitose, $C_{18}H_{32}O_{16}$.

3. Polysaccharides.—

(*a*) *Crystallizable Polysaccharides.*—Gentianose (from *Gentiana lutea*); lactosin (from *Silena vulgaris*); and stachyose (from *Stachys tuberifera*).

(*b*) *Uncrystallizable Polysaccharides.*—These include three sub-groups of related compounds:

Starches, lichenin (from Iceland moss), inulin (from *Inula helenium*), triticin, and glycogen (or animal starch).

Dextrine (or artificial gum), natural gums (including gum arabic, wood-gum, bassorin, etc.), and pectin substances.

Cellulose, lignin, and tunicin (or animal cellulose).

The monosaccharides as a class are neutral, taste sweet, and are colorless and odorless. They are all easily soluble in water, difficultly soluble in absolute alcohol, and insoluble in ether. They are easily oxidizable, and therefore all reduce alkaline solutions of metallic salts. The solution usually taken for this reaction is an alkaline solution of copper tartrate known as "Fehling's solution." This reaction takes place quantitatively, and hence Fehling's solution serves as a means of estimating sugars.

The directions of the U. S. Pharmacopœia for its preparation are: "Dissolve 34.64 Gm. of carefully selected, small crystals of pure cupric sulphate, showing no trace of efflorescence or adhering moisture, in a sufficient quantity of water to make the solution measure, at or near

15° C., exactly 500 C.c. Keep this in small, well-stoppered bottles. Dissolve 173 Gm. of potassium and sodium tartrate, and 125 Gm. of potassium hydrate, in a sufficient quantity of water to make the solution measure, at or near 15° C., exactly 500 C.c. Keep the solution in small, rubber-stoppered bottles. For use, mix exactly equal volumes of the two solutions at the time required. One cubic centimeter of the mixed solution is the equivalent of:

	Gramme.
Cupric sulphate, crystallized, $CuSO_4 + 5H_2O$	0.03464
Cupric tartrate, $CuC_4H_4O_6 + 3H_2O$	0.03685
Glucose, anhydrous, $C_6H_{12}O_6$	0.00500"

Very characteristic for the monosaccharides is the reaction with phenyl-hydrazine, $C_6H_5.NH.NH_2$. When this reagent in dilute acetic acid solution is heated with these compounds, these form difficultly soluble and crystalline *osazones*, by means of which they can be separated and identified.

The monosaccharides are not equally subject to the decompositions in the presence of micro-organisms known as "fermentations." The trioses, hexoses, and nonoses appear to be readily fermentable, while the pentoses, heptoses, and octoses are not decomposed.

The trioses, tetroses, and pentoses are not of sufficient importance to require more than the mention already given in the classification. The hexoses, however, include not only a number of important, naturally occurring sugars, but compounds obtained in the hydrolysis of the di-, tri-, and polysaccharides.

Mannose, $C_6H_{12}O_6$, is obtained by the careful oxidation of mannite, and by the hydrolysis by means of dilute sulphuric acid of many natural carbohydrates, such as salep mucilage and hemicellulose from vegetable ivory-nuts, palm-nuts, etc. Hard, friable powder, easily soluble in water, and fermentable with yeast.

Glucose, $C_6H_{12}O_6$.—This is the most widely distributed of the hexose class. It occurs, under the common name of "grape sugar," along with fructose (fruit sugar) in most sweet fruits and juices. Grape juice contains 10 to 30 per cent., figs 12 per cent., sweet cherries 9 to 10 per cent., apples and pears 7 to 10 per cent., plums and apricots 2 to 5 per cent. Small amounts of this sugar are found in the blood as well as in most of the organs and tissues of the body. In the disease known as "diabetes mellitus" the urine contains larger amounts (as high as 8 to 10 per cent.). It is most readily prepared by the hydrolysis (inversion) of the carbohydrates of the higher classes like cane sugar, which yields a mixture of equal molecules of glucose (dextrose) and fructose (levulose), and starch, which yields products like dextrin and maltose, which gradually pass into glucose. The commercial glucose (or starch sugar) is, however, never perfectly converted, and contains, besides dextrine and maltose, unfermentable sugars as alterative products.

Glucose crystallizes out of alcohol or from concentrated aqueous solution at 30°–35° in anhydrous needles or hard crusts, which fuse at 146°. At ordinary temperatures it crystallizes out of aqueous solution with 1 molecule of water in warty masses. It is distinctly inferior in sweetness of taste to cane sugar.

Galactose, $C_6H_{12}O_6$, is produced along with glucose by the hydrolysis of milk sugar as well as from many other carbohydrates, such as gums. Is also obtained as a decomposition product of the cerebrin of the brain. Crystallizes in small crystals, fusing at 168°, and is fermentable.

Fructose, $C_6H_{12}O_6$, known also as Fruit sugar or Levulose, is found along with glucose, and at times with cane sugar, also in ripe fruits, also found in honey. By boiling cane sugar with dilute acids equal molecules of dextrose and levulose are produced. It is also formed by the decomposition of inulin with dilute acids. Forms a syrup or needles, which unite to rounded aggregates, and fuse at 95°. Tastes sweet, and is lævo-rotatory. Is fermentable by yeast, but more slowly than glucose. It forms a difficultly soluble compound with calcium oxide, $C_6H_9(CaOH)_3O_6$, by means of which it can be separated from the more soluble dextrose compound when the two are present together, as in invert sugar.

Levulose has recently been introduced into medicine under the name of "diabetin," and is made from invert sugar, as indicated above.

Acrose, $C_6H_{12}O_6$ (so named because prepared from acroleïn), is an artificial sugar first made by Emil Fischer, and is interesting as having yielded by various synthetical reactions three other artificial sugars,—mannose, glucose, and fructose.

The heptoses, octoses, and nonoses have as yet only a theoretical interest.

The disaccharides are a most important class, and include several of the best known of the sugars. Under the group hexabioses we have sucrose, or cane sugar, lactose, or milk sugar, and maltose, or malt sugar, as the most important. All these sugars are capable of inversion or hydrolysis in the presence of dilute acids as well as certain ferments, and then yield products belonging to the class of monosaccharides. Thus, sucrose, on inversion, yields a mixture of dextro-glucose and fructose; milk sugar yields dextro-glucose and galactose; and maltose yields dextro-glucose alone. Milk sugar and cane sugar are not fermentable with yeast until after inversion; maltose is directly fermentable. Cane sugar has no effect upon Fehling's solution, while milk sugar and maltose have a reducing effect.

Sucrose (or Cane Sugar), $C_{12}H_{22}O_{11}$ (**Saccharum,** U. S. P.), is very widely distributed in nature, especially in the sugar-cane (*Saccharum officinarum*), which contains from 16 to 20 per cent.; in the sugar-beet, which contains from 12 to 16 per cent.; in the sorghum-cane, which contains from 7 to 10 per cent.; in the sugar-maple, the juice of which contains from 3 to 4 per cent.; in Indian corn, and in many fruits. The extraction and commercial manufacture is practically limited to the two sources first named, the sugar-cane and the sugar-beet. An outline of the process of manufacture will be appended to this section.

Pure sucrose crystallizes in anhydrous, monoclinic crystals, melting at 160°. Easily soluble in water, difficultly soluble in alcohol, insoluble in ether, chloroform, or carbon disulphide. Is dextro-rotatory, its specific rotatory power being $+66.5°$ for rays $[a]_D$.

The optical analysis of sugar solutions is effected by the aid of the polariscope (see p. 80), an instrument in which the ray of polarized light is made to pass through a definite length (usually 100 or 200 mm.) of a solution made up by dissolving a definite weight of the sugar (26.048 gm. in most instruments) in 100 c.c. of pure water, and filtering if necessary. The plane of the ray is rotated thereby through a certain angle, and on rotating the analyzing prism of the polariscope through a corresponding angle in the opposite direction the effect is just compensated for. The circular scale on the tube rotated is graduated in percentage numbers, so that the percentage strength of the sample in pure sugar can be read off at once.

Cane sugar does not reduce Fehling's solution, nor is it directly fermentable with yeast, as is glucose. Prolonged contact with the yeast, however, brings about an inversion through the action of the soluble ferment *invertin* present in the yeast, and then the products of the inversion, dextrose and levulose, at once ferment. Cane sugar unites with lime and strontia to form insoluble saccharates, such as $C_{12}H_{22}O_{11} + 3CaO$ and $C_{12}H_{22}O_{11} + 2SrO$. Concentrated sulphuric acid dehydrates and chars the sugar, producing a coke. Prolonged action of dilute hydrochloric acid converts sugar into levulinic acid (see p. 614).

Lactose, or Milk Sugar, $C_{12}H_{22}O_{11}+H_2O$ (**Saccharum Lactis, U. S. P.**).—This variety of sugar occurs in the milk of the mammalia to the extent of from 3 to 6 per cent., and is usually obtained from the "whey" or thin liquid which remains when the casein has been coagulated by rennet. It crystallizes in hard, white crystals with 1 molecule H_2O. It is less sweet than cane sugar, and less soluble in water; insoluble in alcohol, ether, and chloroform. It is dextro-rotatory, $[a]_D=52.5°$. It differs from cane sugar in having a direct reducing power on Fehling's solution.

Maltose, $C_{12}H_{22}O_{11}$, results from the action of the diastase of malt upon starch during the germination of cereals (as in malting of grain), and also as an intermediate product on boiling starch with dilute sulphuric acid. It forms fine, white needles, crystallizes with 1 molecule of H_2O, and is easily soluble in water. It is strongly dextro-rotatory, $[a]_D=+137°$. It reduces Fehling's solution, the reducing power being about two-thirds that of glucose, is easily decomposed by alkalies, is fermented with yeast, and yields on hydrolysis with dilute acids only dextro-glucose. Neither maltose nor lactose reduces Barfoed's reagent (an acetic acid solution of copper acetate), and in this way may be distinguished from glucose.

Isomaltose, $C_{12}H_{22}O_{11}$, is formed synthetically from dextro-glucose by the prolonged action of strong hydrochloric acid at 10°–15°, and is contained in commercial starch sugar because of such retrograde action. It is also a product of the action of diastase upon starch, and is present in malt; as it undergoes fermentation only slowly, it is usually present unchanged in fermented malt liquors, such as beer (amounting to 25–30 per cent. of the beer extract at times). It is intensely sweet, and changes at 65° into yellowish-brown products of roasting, which are also sweet and give character to the roasted malt.

The most important trisaccharide or hexotriose is

Melitriose or Raffinose, $C_{18}H_{32}O_{16}$.—This sugar is found in the sugar-beet, and hence obtained in the working of the molasses from the same; also in the Eucalyptus manna, in cotton-seed cake, etc. Is less soluble in water than cane sugar, and almost devoid of sweet taste. Strongly dextro-rotatory, $[a]_D=103.[illegible]°$. It does not reduce Fehling's solution. Readily fermentable with yeast. When inverted, yields first fructose and melibiose.

and the latter is then decomposed into galactose and dextroglucose.

The crystallizable polysaccharides mentioned are as yet of slight importance. The uncrystallizable polysaccharides, on the other hand, include compounds of the greatest importance in the growth of vegetable life, and as the basis of food preparations used for human sustenance.

Starch, $(C_6H_{10}O_5)_n$ (**Amylum**, U. S. P.), is very widely distributed, being contained in all assimilable plants, in which it constitutes a reserve material. As such it is contained especially in the roots, tubers, seeds, fruit, and in the medullary rays of the trees during the winter. During the movement of the sap of the plant it is changed into sugar. Starch is extracted practically from potatoes (containing 21 per cent.), from maize or Indian corn (containing 50 per cent.), from wheat (containing 64 per cent.), and from rice (containing 77 per cent.). Specially rich in starch also are the tropical plants, such as arrow-root, sago, and manihot.

Starch consists of a white, velvety, somewhat hygroscopic powder, recognized under the microscope as made up of granules of round or slightly elongated shape which show a concentric structure. The interior substance of the granule, or the true starch material, is called "granulose," and is readily dissolved under the action of diastatic ferments, while the exterior shell is a cellulose material called "farinose," and is not acted upon by ferments.

The most complete classification of the starches is that of Muter as amplified by Blyth, by which they are divided into five groups, on the basis of their physical and microscopical differences, as follows:

(*a*) *The potato group* includes such oval or ovate starches as give a play of colors when examined by polarized light and a selenite plate, and have the hilum and concentric rings clearly visible. It includes *tout les mois*, or canna arrow-root, potato starch, maranta, or St. Vincent arrow-root, Natal arrow-root, and curcuma arrow-root.

(*b*) *The leguminous starches* comprise such round or oval starches as give little or no color with polarized light, have concentric rings all but invisible, though becoming apparent in many cases on treating the starch with chromic acid, while the hilum is well marked and cracked, or stellate. It includes the starches of the bean, pea, and lentil.

(c) *The wheat group* comprises those round or ov
having both hilum and concentric rings invisible in t
of granules. It includes the starches of wheat, b
chestnut, and acorn, and a variety of starches from
plants, such as jalap, rhubarb, senega, etc.

(d) *The sago group* comprises those starches of w
granules are truncated at one end. It includes sag
and arum, together with the starch from belladonna,
scammony, podophyllum, canella, aconite, cassia, and

(e) *The rice group.* In this group all the starche
lar or polygonal in form. It includes the starches of
buckwheat, maize, dari, pepper, as well as ipecacuanh

In addition to the differences in form and marking
above, the starch-granules differ in size according to
ent sources, so that under the microscope they can
guished by the measurement of the average diame
granule. This ranges, according to Karmarsch, from
millimeter, or from .0004 to .0079 inch.

Fig. 97 illustrates some of the most characteristi
starches as seen under the microscope.

Starch is insoluble in cold water, alcohol, and ether
ing with water it begins to swell up at 55° C., and at
the granules burst and it becomes a uniform, transl
known as "starch paste," which is not, however,
as the water can be frozen out of it. Boiled with
long time it goes into solution, one part dissolving in
of water. The prolonged action of glycerin at 190°
the change into *soluble starch.* The action of heat
is to change it gradually into dextrine, which is solu
water. Both the starch-granules and the starch paste
intensely blue by iodine. The compound formed
addition compound, and the blue color disappears
but returns again on cooling. This starch reaction
indicate the existence of the starch molecule in any
extract, and the gradual breaking down of this mole
the influence of hydrolysis can also be checked off
the iodine reaction. Thus, under the influence of
dextrin and dextrose are produced, the latter eventu
product. Many ferments, like saliva, the pancreati
and especially the diastase of malt, produce in the star
what similar change, and yield maltose, $C_{12}H_{22}O_{11}$, an
of intermediate products between this and starch. The

and the distinguishing tests by which they may be recognized may be stated as follows :

Starch		gives a blue iodine reaction.
Soluble starch (amylo-dextrine)		gives a blue iodine reaction.
Dextrines	Erythro-dextrine	gives a violet and red iodine reaction.
	Achroo-dextrine	gives no iodine reaction.
	Malto-dextrine	gives no iodine reaction.
Maltose		reduces Fehling's solution but not Barfoed's reagent.
Dextrose		reduces Fehling's solution and also Barfoed's reagent.*

Strong nitric acid in the cold acts upon starch, producing nitro derivatives, such as mono-, di-, and tetra-nitro-amylose, collectively known as xyloïdin.

Lichenin is prepared from lichens as a gelatinous mass (Iceland moss), soluble in water, and precipitable in flocks on addition of alcohol.

Inulin $(C_6H_{10}O_5)_2$, is obtained from the roots of *Inula helenium*, from the *Dahlia*, *Helianthus*, and other sources. Forms a white powder made up of microscopical spherules. Easily soluble in water and in copper oxide-ammonia (Schweizer's reagent). Does not reduce Fehling's solution, but does reduce ammoniacal silver solution.

Glycogen, $(C_6H_{10}O_5)_n$.—Known also as animal starch. Is found most abundantly in the livers of mammalia and in notable quantities in the tissues of the embryo. White, amorphous powder, soluble in water to an opalescent dextro-rotatory liquid, which is colored red with iodine. After the death of the animal the glycogen changes to dextrose very rapidly, and the same change takes place when it is boiled with dilute acids, while ferments change it into maltose.

Dextrine, $(C_6H_{10}O_5)_2$.—This substance can be formed from starch by the action of dilute acids, of diastase, or by heat alone. In the latter case the reaction is merely one of molecular rearrangement, and may be approximately expressed by the reaction $2(C_6H_{10}O_5)_3 = 3(C_6H_{10}O_5)_2$. In the other cases it is probable that hydrolysis gives rise to several successive changes, and different dextrines are considered as being formed successively, such as *erythro-dextrine*, *achroo-dextrine*, and ***malto-dextrine***. Technically, dextrine is obtained by the heating of starch after moistening with dilute acids. Dextrine is a white or yellowish-brown powder, readily soluble in water, from which solution it may be precipitated on addition of alcohol. Gives a red color with iodine.

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[*] Sadtler's Industrial Organic Chemistry, p. 163.

Is dextro-rotatory. It does not reduce Fehling's solution nor Barfoed's reagent. It is not directly fermentable, but in the presence of diastase it goes over into fermentable products. Dextrine is used as a substitute for the natural gums in calico-printing and manufacture of textile goods for a stiffening material, and for glazing paper and card-board, and enters into many food products.

The natural gums are a class of vegetable products which occur at times as amorphous, translucent, or transparent exudations, as in the case of gum arabic, or are extracted by dilute alkalies from the plants, and then are thrown out of solution on addition of hydrochloric acid and alcohol, as in the case of the wood-gums. These gums are soluble in water, forming thick, sticky solutions, which can be filtered, however. They do not reduce Fehling's solution, but by heating with dilute acids yield monosaccharides like arabinose, xylose, dextrose, and galactose.

Somewhat similar products, but only partially soluble in water, are the vegetable mucilages. These do not dissolve, but swell up with water to form liquids which cannot be filtered.

Gum Arabic (Arabin or Calcium Arabate).—This substance (**Acacia,** U. S. P.) is an exudation from the acacia and mimosa species of Africa and the Orient. It contains about 3 per cent. of ash, and on adding hydrochloric acid to the aqueous solution and precipitating with alcohol, a colorless, amorphous substance is obtained. This is arabic acid. On hydrolysis it yields galactose, arabinose, and a pentabiose named arabinon. The so-called "metapectic acid," from the pulp of the sugar-beet, is considered to be identical with arabic acid.

Related to the acacia gums are *wood-gum*, from the wood of foliage trees, yielding xylose on hydrolysis; *cherry-gum*, the gum of cherry- and almond-trees, yielding *l*-arabinose on hydrolysis; *peach-gum*, from the peach-tree, yielding arabinose and galactose on hydrolysis; *barley-gum*, obtained in the nitrogen-free extractive material of cereals, yielding galactose and xylose.

Bassorin is the mucilaginous constituent of gum bassorin and gum tragacanth (**Tragacantha,** U. S. P.).

Carragheen is the mucilaginous constituent of Irish moss (**Chondrus,** U. S. P.). Is not precipitated from its solutions on addition of alcohol; yields galactose on hydrolysis with dilute sulphuric acid. The pectine substances which are found in certain fruits like apples and pears, and in fleshy roots like the beet and the carrot, are also closely related to the carbohydrates. Their concentrated solutions gelatinize on cooling.

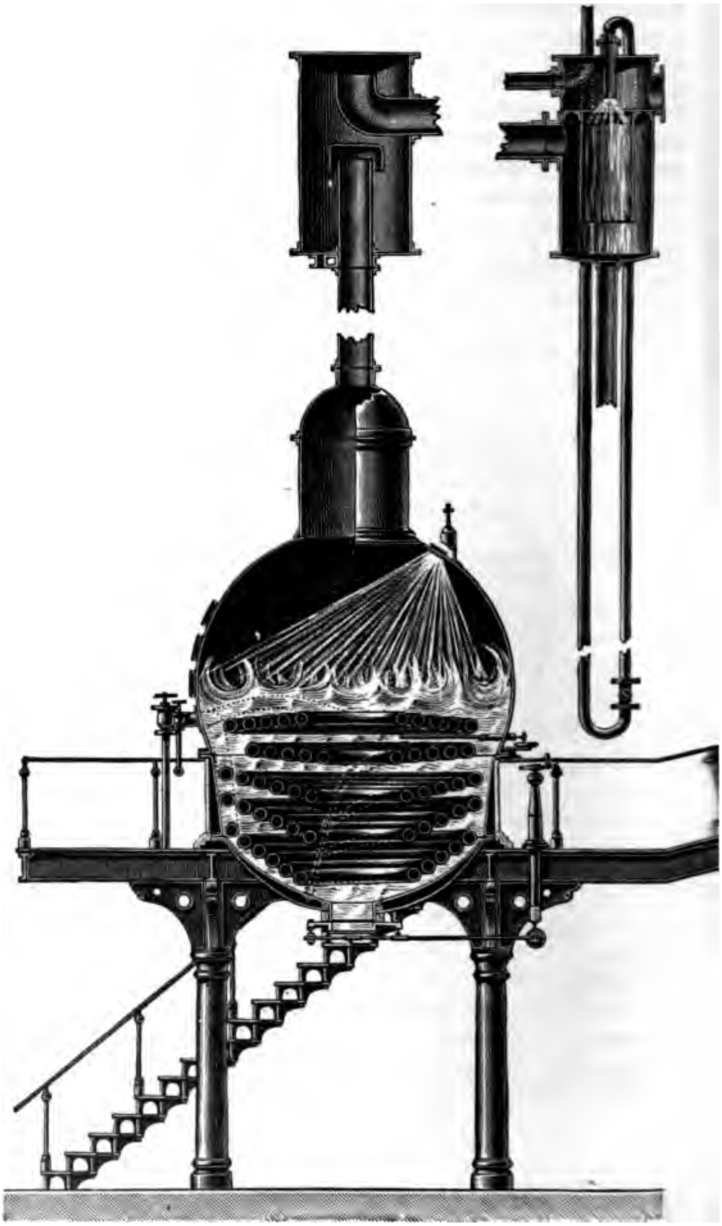
Cellulose is the name given to the material of which the growing plant-cell is composed; as the membrane becomes older incrustations of mineral salts occur, and the cellulose also undergoes partial change into lignin, a closely related substance.

Cellulose is insoluble in the ordinary solvents, and therefore to prepare it in a state of purity the plant-fibres like cotton and flax are treated successively with water, alcohol, ether, dilute alkalies, dilute hydrochloric and hydrofluoric acids. The residual fibre is then chemically pure cellulose. We have an example of this in Swedish filter paper, which has been prepared in this way for quantitative analytical use. The cotton fibre is also conveniently purified, and then furnishes a very pure cellulose (**Gossypium Purificatum, U. S. P.**). Pure cellulose is amorphous, and, as stated, insoluble in ordinary solvents. It is soluble, however, in an ammoniacal solution of cupric hydrate (Schweizer's reagent), and is thrown out of this solution on addition of acids and salts. After washing with alcohol it forms a white, amorphous powder. Boiling with dilute acids converts it into dextrine and dextrose, while concentrated sulphuric acid converts it into *amyloid*, an amorphous, translucent mass.

In the manufacture of parchment-paper advantage is taken of this amyloid formation. Unsized paper is passed rapidly through strong sulphuric acid, which causes a superficial change of the cellulose into amyloid; the paper is then washed with water to free it from the adhering acid and hung up to dry. The paper is thus made much stronger and less pervious to liquids, as the pores are filled with the colloidal cellulose.

A mixture of nitric and sulphuric acids has a "nitrating effect," and gives rise to a series of nitric esters or so-called "nitrocelluloses." Taking the formula of cellulose as $C_{12}H_{20}O_{10}$, we have a series beginning with a dinitrate, $C_{12}H_{18}O_8(NO_3)_2$, and running to the hexanitrate, $C_{12}H_{14}O_4(NO_3)_6$. Of these the highest (the hexanitrate) constitutes the true explosive *gun-cotton*, and is insoluble in alcohol, ether, or a mixture of the two. A mixture of the tetranitrate and the trinitrate, on the other hand, constitutes **Pyroxylin, U. S. P.**, and is soluble in a mixture of alcohol and ether, the solution forming **Collodion, U. S. P.** In the preparation of this latter the Pharmacopœia prescribes the dissolving of 30 gms. of pyroxylin in a litre of the solvent, made up of 3 parts of ether and 1 part of alcohol. From this solution on evaporation of the solvent the proxylin is left as a transparent, flexible film.

FIG. 98.

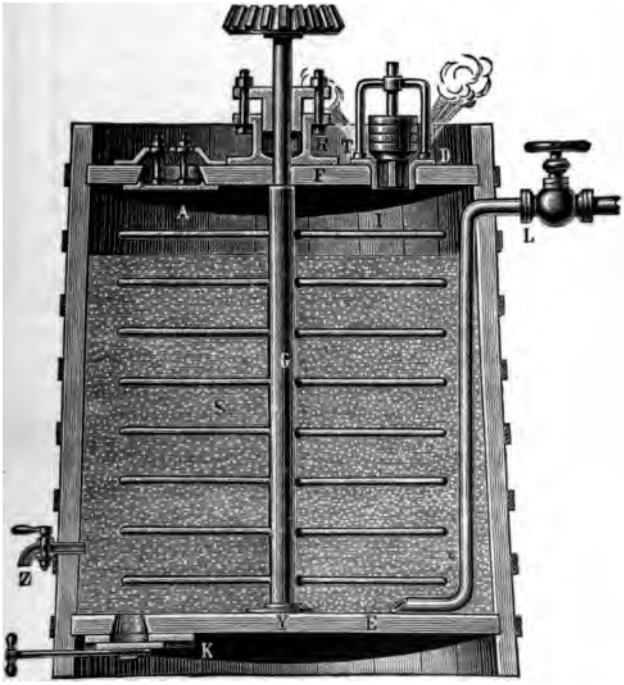


Vacuum-pan.

ar-beet, is essentially the same. The raw sugars are "melted," that dissolved in hot water, and then the solution is defecated with the aid blood albumen, filtered through bag-filters (or filter-presses in the case beet sugar), and then through bone-black, from which it comes prac-lly colorless. It is then evaporated in vacuum-pans to the crystal-ng point or "strike," and allowed to cool and thoroughly crystallize. e magma of crystals and syrup is then put into a centrifugal and the up separated. The grocery sugars are ready for barrelling as they ne from the centrifugal, while the white crystal sugars are dried by a rent of hot air before being finished.

. **The Manufacture of Commercial Glucose.**—This is made exclusively n starch by the action of dilute acids, and in this country the starch d is that obtained from Indian corn. Sulphuric acid is generally ployed, and the inversion of the starch is carried out in either open closed "converters." A form of closed converter early used in the cose industry is seen in Fig. 99. The amount of oil of vitriol used is

FIG. 99.



Manufacture of glucose.

m one-half pound to one and a quarter pounds per hundred pounds of rch. The starch and water are taken of a gravity of from 18° to 21° B., l the pressure amounts to from forty-five to seventy-five pounds per square inch. In the manufacture of "glucose syrup," the conversion is not so complete, and the quantity of dextrine is larger than where the solid "grape sugar" is to be obtained as the product. Anhydrous crystallized dextrose can also be obtained as the end product of this inversion of starch by Dr. Behr's patent.

3. **The Manufacture of Starch.**—Starch is obtained commercially from Indian corn, from wheat, and from potatoes. As made from corn in this country, the corn is first steeped in water at a temperature not exceeding 140° F. for from three to ten days, the water being renewed frequently. The softened corn is then ground between burr-stones, while a stream of water is kept running continuously into the hopper. As it is ground, the thin paste is carried on to a series of rotating or shaking sieves. The magma so obtained is then run over inclined sieves of silk bolting-cloth, when the starch goes through as a milky liquid, and is run into settling vats. It is here treated with a weak alkaline solution, to dissolve and remove the gluten, oil, etc., and thoroughly washed by agitation and decantation. It is finally allowed to settle, and dried first in boxes with perforated bottom, and then upon plaster of Paris supports while dried with warm air. 56 lbs. of corn in this way are made to yield 28 lbs. of purified starch. In the manufacture of starch from wheat, the large amount of gluten makes it necessary to take measures to remove it. This is done in the "sour" process by fermentation, the acetic and other organic acids produced rapidly dissolving the gluten and liberating the starch-granules.

4. **The Manufacture of Paper from Cellulose.**—The materials utilized in paper-making are all cellulose-containing substances, such as linen and cotton rags, esparto grass, straw, jute, manila, and wood-fibre. The first chemical treatment after the mechanical preparation of the material is ordinarily the boiling with caustic alkali. In the case of the rags, this has the effect of thorough cleansing; in the case of esparto, straw, etc., it combines with the resin and silica, liberating the cellulosic fibre; in the case of wood, however, the action is necessarily a more fundamental one, as the true cellulose is not only incrusted with mineral matter, but combined with lignin. In the preparation of chemical wood-pulp, however, there are two distinct processes, the "soda-pulp process" and the "sulphite process." In the former, the chipped wood is digested under several atmospheres' pressure with caustic alkali to effect its disintegration; in the latter, calcium or magnesium bisulphite is used, also under considerable pressure, to effect this disintegration. After a thorough washing of the disintegrated pulp, it may be bleached if intended for white paper. This is done with bleaching-powder solution, the excess of chlorine being removed with hyposulphite of soda, known, therefore, as "antichlor." The bleached pulp is then mixed with the proper filling material and sizing, and is ready to go to the "fourdrinier" or paper machine.

5. **The Manufacture of Gun-cotton, Pyroxylin, and Celluloid.**—In the manufacture of the true gun-cotton, the maximum of nitration is sought, and the nitrating mixture is hence of the strongest nitric and sulphuric acids, in the proportion of 3 parts of the latter to 1 part of the former. This acid mixture is cooled first, and then the cotton is immersed and left

residue. The density of celluloid ranges from 1.310 to 1.393. When heated to 125° C. it becomes plastic, and can be moulded into any desired shape.

X. FERMENTATION AND FERMENTATION INDUSTRIES.

We include under the name of fermentations certain methods of decomposition of organic compounds which presuppose the presence of definite substances called "ferments," which do not, however, apparently take part in the chemical reactions. Their presence in relatively small amount suffices to bring about the decomposition of large quantities of the fermentable material.

The ferments which seem to determine the decomposition may be either soluble unorganized ferments or insoluble organized ferments, which are minute vegetable growths. The decompositions which are brought about by organized ferments differ quite notably in their results from those which can be induced by mere chemical reagents. Thus, the decomposition of sugar into alcohol and carbon dioxide, as it is brought about by the activity of the living yeast-cell, cannot be brought about by purely chemical treatment. On the other hand, the action of the unorganized ferments is much more analogous to that induced by chemical reagents. Thus, the hydrolytic action of diastase on starch can also be perfectly imitated by treating with dilute acids. A distinction is therefore sometimes made between "true distinctive fermentations" and "fermentative decompositions."

With regard to the chemical nature of the *enzymes*, or soluble ferments, we only know that they belong to the class of proteids. A recent analysis of diastase by Lintner may be taken as typical of the class: carbon, 46.66 per cent.; hydrogen, 7.35 per cent.; nitrogen, 10.42 per cent.; sulphur, 1.12 per cent.; and oxygen, 34.45 per cent.

While soluble in water and glycerin they are insoluble in alcohol, and are precipitated from aqueous solution on addition of lead acetate. Their activity is destroyed by heating, that of diastase at 75° C., and all by boiling with water. Their activity is not destroyed by the presence of antiseptics, which arrest the action of the organized ferments. Thus, chloroform, thymol, and salicylic acid will all arrest the activity of the organized growth but not interfere with that of the soluble ferments. Sodium fluoride in 1-per-cent. solution is said to entirely check the growth of the organized ferment, but is without action on those which are soluble.

found in the pancreatic juice, both have what is termed a "proteolytic" power, or ability to digest or decompose proteid matter.

Pepsin, U. S. P., is described as "a proteolytic ferment or enzyme obtained from the glandular layer of fresh stomachs from healthy pigs, and capable of digesting not less than 3000 times its own weight of freshly coagulated and disintegrated egg albumen." It is obtained as a fine white or yellowish-white powder or in scales or grains, soluble in water or glycerin, but insoluble in alcohol. It can bear a dry heat of 110° without losing its activity, but heated with acidulated water to 100° it is deprived of all proteolytic power. The products which result from the action of pepsin and trypsin upon albuminoid material are called *peptones.* The pancreatic juice contains besides the trypsin another soluble ferment known as *steapsin,* which has the power of emulsifying and partially saponifying fats. The mixture of enzymes naturally existing in the pancreas of warm-blooded animals and usually obtained from the fresh pancreas of the hog is the **Pancreatinum,** U. S. P.

Corresponding to these peptonizing ferments of animal origin is a vegetable ferment, *papaïn,* obtained from the milky juice of *Carica papaya.* It is a white, amorphous powder, soluble in water and glycerin. It peptonizes proteids very readily, acting like trypsin. It is claimed for it, moreover, that it digests and removes the membrane of croup and diphtheria.

The ferment which is extracted from the mucous membrane of the stomach, and which has the power of coagulating the casein of milk, has been called *rennin* (or présure). The preparation called rennet is usually obtained from the stomach of the calf.

Urease is the name given to the enzyme which, equally with organized ferments, is capable of bringing about the ammoniacal fermentation. The reaction for the decomposition of urea is $CO(NH_2)_2 + 2H_2O = (NH_4)_2CO_3$.

A few additional enzymes have been specifically studied, such as *pectase,* characteristic of the pectic fermentation of fruits, etc.

The organized ferments or vegetable growths may be divided into three classes: first, mould growths; second, yeast-plants, or the different species and varieties of *Saccharomyces;* and third, bacteria, belonging to several different genera.

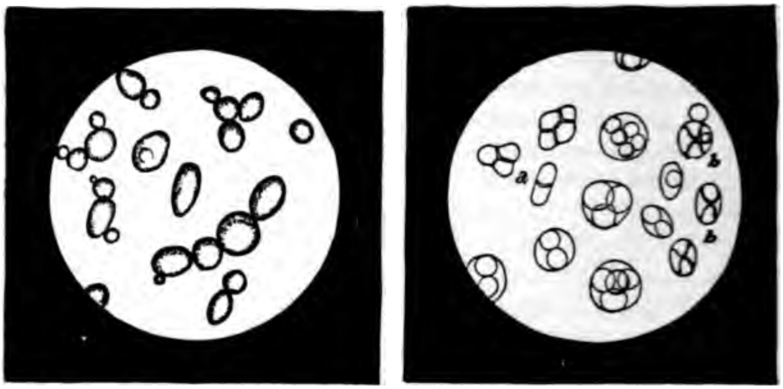
The mould growths at times are able to induce fermentations, but their action consists much more in secondary changes effected in the fermenting bodies or the products of fermentation. *Penicillium glaucum,* the most widely distributed mould growth, is capable of bringing about a number of chemical decompositions. It is said to furnish a soluble ferment capable of inverting cane sugar. *Aspergillus glaucus* possesses a diastatic ferment. For the preparation of the Japanese saké (or rice-wine) is used the *Aspergillus oryzæ*, which comes on the rice grains. The varieties of Mucor (*M. racemosus* and *M. mucedo*) develop some degree of fermentation in dextrose, invert sugar, and maltose. *Oidium lactis* is found in milk.

Much the best defined of all these changes, however, is the alcoholic fermentation as developed by the activity of the yeast-plant. As before stated, it is sugars of the formula $C_6H_{12}O_6$ that are directly acted upon. According to Pasteur, about 95 per cent. of the sugar is decomposed, according to the reaction $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$, while the rest is decomposed according to secondary reactions, yielding a variety of products, of which glycerin and succinic acid are the most notable. This most important reaction is developed by the species of the genus *Saccharomyces*. The species *Saccharomyces cerevisiæ* is recognized as the special ferment of beer, while *Saccharomyces ellipsoideus* is the ferment of wine. Of the *S. cerevisiæ*, moreover, two well-characterized varieties can be distinguished. The first of these is most active at ordinary temperatures (16°–20° C.), and develops its full fermentative activity in the course of 3 to 4 days; the second develops its activity at a lower temperature (6°–8° C.), and the action is much slower. The first of these yeast-plants, placed in a sugary liquid, is brought by the liberated carbon dioxide to the surface, and hence is said to develop a surface fermentation, while the second remains at the bottom during its whole activity, and the action is called a bottom fermentation. Upon the use of these two varieties are based two quite distinct methods of beer brewing.

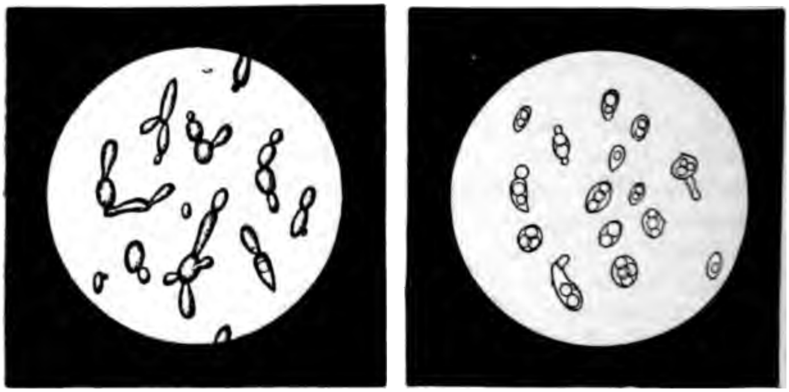
Within recent years much attention has been paid to pure cultures of the yeast-plant, and in this way much more regular and uniform fermentations have been produced with the result in a better product. This work has been done largely by Hansen, of Copenhagen, and the microscopical appearance of three of these pure cultures and the ascospore formation of the same are shown in Fig. 100. Of these illustrations, the *Saccharomyces cerevisiæ* and *S. pastorianus* are beer ferments, while *S. ellipsoideus* is the wine ferment.

The special conditions of the alcoholic fermentation are: first, an aqueous sugar solution containing 1 part of sugar to from 4

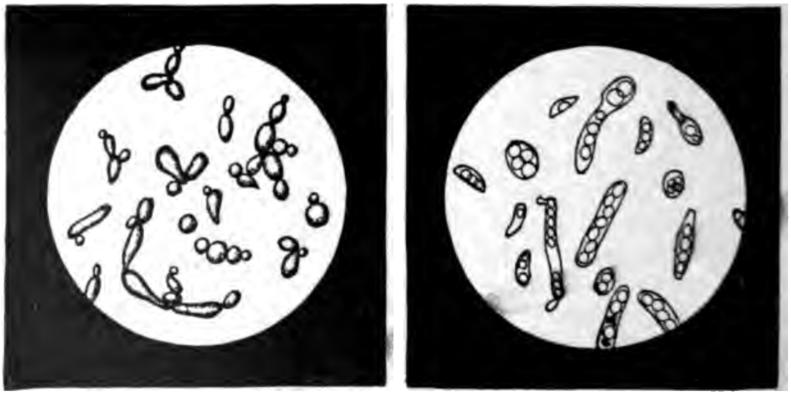
FIG. 100.



Saccharomyces cerevisiæ. **Saccharomyces cerevisiæ. Ascospores.**



Saccharomyces ellipsoideus. **Saccharomyces ellipsoideus. Ascospores.**



Saccharomyces **pastorianus.** **Saccharomyces pastorianus. Ascospores.**

to 10 parts of water. Second, the presence of a yeast ferment. If this is not added in already developed and active condition, or if the fermentation is to be a spontaneous one,—that is, brought about by the spores present in the air,—the conditions for the growth of the yeast-spores must be present; the solution must contain protein material and phosphates of the alkalies and alkaline earths. Third, the temperature must range between the limits 5°–30° C., or, more narrowly, 9°–25°. Above 30° the butyric fermentation tends to develop rather than the alcoholic, and other decompositions ensue.

The number of changes brought about by organized ferments of the third class or bacteria is very great. Thus, *Bacillus subtilis*, *B. amylobacter*, and *B. termo* bring about a peptonization of albuminoids which, under the influence of these bacteria, decompose into leucin, tyrosin, and ammonia. The butyric acid ferment seems to be the starch-converting *Bacillus amylobacter* (*Clostridium butyricum*, *Vibrio butyricus*), although butyric acid [illegible] not the only product developed by it. Under the influence of this bacterium, along with butyric acid, starch solutions yield dextrine and sugar. *Bacterium termo* develops, also, a general putrefaction. As lactic acid ferments, a number of bacteria, which have been only partially studied, are designated. The ones most widely distributed are *Bacillus acidi lacti* and *Micrococcus prodigiosus*.

The acetic fermentation is developed by at least three kinds [illegible] bacteria. *Bacterium aceti* was discovered by Pasteur, while Hansen has found two additional acetic ferments, *Mycoderma cerevisiæ* and *Mycoderma pasteurianum*, the latter being the most characteristic.

A series of bacteria which develop turbidity in beer as well as [illegible] unpleasant odor and taste are known collectively as "Sarcina." The most important of them, discovered by Lintner, is *Podiococcus cerevisiæ*.

The acetic fermentation is that which most readily develops from the alcoholic and follows it often as a spontaneous change. It requires, besides the presence of a dilute alcohol or alcohol containing liquid, the presence of nitrogenous compounds and salts, and is, above all, what is termed an aërobic fermentation,—that is, requires the presence of oxygen. The temperature most favorable for the development of the acetic ferment is between 18° and 35° C. The reaction is purely one of oxidation, $C_2H_6O + O_2 = C_2H_4O_2 + H_2O$, and can be brought about by chemical means, such as the action of platinum black on dilute alcohol, etc.

The lactic fermentation takes place without the necessity of oxygen, and hence is termed an *anaërobic* fermentation. It takes place in neutral or alkaline solutions, and is hindered by the presence of small amounts of acid. By it galactose, from the inversion of sugar of milk, is simply decomposed, according to the reaction $C_6H_{12}O_6 = 2C_3H_6O_3$. The most favorable temperature is from 35° to 40° C.

The butyric fermentation is like the lactic, and generally follows it. It is also *anaërobic*. The reaction for the production of butyric acid by this fermentation is $2C_3H_6O_3 = C_4H_8O_2 + 2CO_2 + 2H_2$. Other organic compounds, besides sugar, are capable of undergoing this fermentation. Glycerin, under the influence of bacteria, is decomposed into normal butyl alcohol, normal butyric acid, ethyl alcohol, and caproic acid. As the conditions for the lactic and butyric fermentations, both as to

FIG. 101.

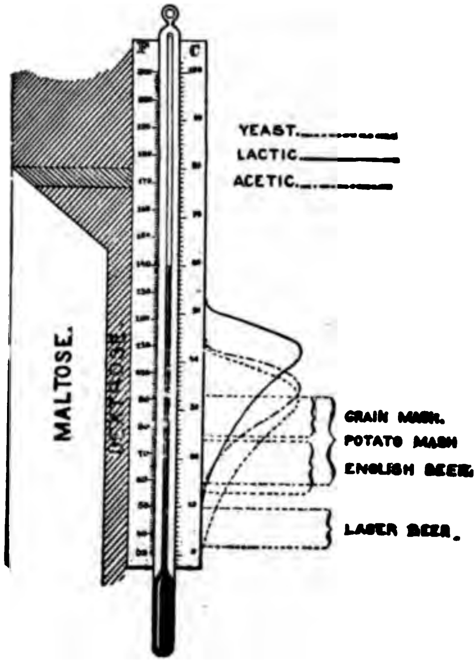


Diagram of temperatures.

temperature and absence of free oxygen, exist in the intestines, these fermentations take place there, the sugars, organic acids, soluble proteids, and mucus being the material acted upon. The products, as seen in the reactions above, are lactic and butyric acids and carbon dioxide and hydrogen gases. These gases distending the bowel produce the painful symptoms of colic, etc.

The effect of temperature upon the several ferments is shown in the graphic illustration Fig. 101, as well as the influence of temperature upon the decomposition of starch by diastase. On the right side of the figure the regularly-dotted line represents the yeast curve. As the temperature rises from 0° C. its activity increases until the maximum is reached at about 33° C., when it diminishes again, and at 50° or thereabouts it is killed. The activity of the acetic ferment is represented at the same time by the irregularly-dotted line, and that of the lactic ferment by the black line.

FERMENTATION INDUSTRIES.

The most important industrial utilizations of the results of fermentation are those in which the alcoholic fermentation of sugar- and starch-containing materials enters.

1. The Malting and Brewing of Beer, Ale, etc.—Malt liquors, as they are termed, are the products of the fermentation of infusions of malted grain, flavored by the bitter extract from hops, and contain from 3 to 7 per cent. of alcohol, together with extractive matter made up of the peptones from the alteration of albuminoids and the carbohydrates from the alteration of the starch of the original grain. The malting process is carried out so as to allow the barley or other grain to germinate, whereby the character of the albuminoids is changed and the ferment diastase is developed, which then begins to act on the starch, the germination and change being stopped at a certain stage by heating in a kiln. Besides the diastase, a second soluble ferment is formed during the malting process, the so-called "peptase," which in the mash process changes the proteids of the malt into peptones and para-peptones, which give nutritive value to beer. Wheat, corn, and rice are used at times as partial substitutes, but the bulk of the grain used is always barley. The finished malt is always yellow or amber-colored shading to brown. The crushed malt is then put through what is termed the mashing process, which is for the purpose of obtaining an infusion containing maltose and dextrine, as well as to allow the diastase to complete the hydrolysis of the starch, changing it into the products before described under the Carbohydrates. This infusion is then strained off and boiled while the hops are added. The "wort," as the liquid is now called, is then cooled, preparatory to the fermentation. This cooling is effected as rapidly as possible, so that the lactic fermentation and similar changes may not develop, and that the spores of foreign yeast ferments may not have access to the liquid. The thick magma of yeast-cells is then added in the proper amount and the fermentation started, which, as before stated, may be a surface fermentation or a bottom fermentation, according to the temperature and the character of the yeast used. The products differ according to the character of the malt used, whether light or dark, and the character of the fermentation, whether a rapid or a slow one.

2. The Manufacture of Wines.—While the name wine is often used to include products of the spontaneous alcoholic fermentation of any sweet fruit or berry, it is usually limited to the product of the fermentation of the grape, which alone is cultivated on an extensive scale throughout the civilized world for the manufacture of wine. The raw material here is the "must," or expressed juice of the grape, which may be fermented either alone or in contact with the "marc," as the pressed pulp and skins are called. The must contains: first, from 16 to 28 per cent. of fermentable sugar (a mixture of dextrose and levulose); non-nitrogenous extract (pectin substance and salts, chiefly of tartaric acid); albuminoids, and free acids (tartaric, malic, and succinic). The percentages of the sugar and the free acids are the most important elements in deciding the probable value of the wine obtainable from the must. The fermentation is a spontaneous one and a protracted one, as, after the full development of the alcoholic strength of the wine, it is left to ripen and develop by an after-fermentation the fruit essences or esters, which give the flavor and bouquet to the wine. In the case of red wines, the main fermentation is allowed to take place with the marc added to the must, so that as the alcohol is developed it may dissolve out the coloring matter of the skins as well as some of the tannin, which is of benefit in effecting a more rapid separation of the protein materials. During the secondary fermentation these deposit upon the inner walls of the storage casks *argols*, or impure acid potassium tartrate (German, weinstein), with some yeast and albuminoid matter. The first fermentation of the must lasts from 1 to 4 weeks, the secondary fermentation from 3 to 6 months, and then the wine is put into casks to ripen, which continues during from 2 to 8 years.

In the manufacture of champagnes and effervescing wines, after the secondary fermentation is nearly finished a mixture of alcohol and pure cane sugar is added, and the wine is bottled so that the supplementary fermentation may continue and develop alcohol and carbon dioxide again. The pressure which develops from this dissolved gas may rise to from 4 to 5 atmospheres.

The percentage of alcohol by weight in wines varies within wide limits, ranging from 5 per cent. in light Rhine wines to 18 per cent. in sherry and port wine.

3. The Manufacture of Distilled Liquors or Ardent Spirits.—In this industry the effort is made to push the fermentation to the fullest possible limit, so that the maximum quantity of alcohol may be produced, and then this product of fermentation is distilled, and it may be redistilled in order to get a distillate richer in alcohol than the fermentation product itself can be. The end product sought may be either an alcoholic beverage, which is the product of the distillation, or a raw spirit, which is then redistilled and strengthened until the "rectified spirit" is obtained, which is used as the basis of many lines of manufacture for the chemist and the pharmacist. The raw materials for this industry may be: first, alcoholic liquids themselves, products of fermentation, which are to be redistilled (such as wines used for manufacture of brandies); second, sugar-containing materials (such as cane-molasses used for manufacture of rum, and beet-molasses and sweet fruits used for fruit brandies); and third, starch-containing cereals and all materials capable of hydrolysis by diastase and fermentation (such as corn, rye, barley, rice, and potatoes). In case the last-named materials are used, the preparation of the wort is the first step. This is analogous to the method already described under malt liquors, except that the whole of the starch is to be converted if possible into maltose, which is directly fermentable, and the dextrine must be thoroughly changed into sugar. The fermentation of the distiller's wort is also somewhat different from that of the brewer, as the maximum percentage of alcohol is to be attained. The yeast is, therefore, a surface yeast, and a maximum temperature of 33° to 34° is attained.

In case molasses is to be fermented for rum, the fermentation is a spontaneous one, the nitrogenous matters present making the addition of yeast unnecessary.

The product of the first distillation of any of these thoroughly fermented mixtures, especially those obtained from grain mashes, is a "raw spirit," containing sharp, aldehydic constituents on the one hand, and higher alcohols (fusel oil) on the other hand, in addition to the ethyl alcohol. These are, as far as possible, to be eliminated or changed by the process of rectifying, and then by storage the supplementary changes of the higher alcohols into ethers are completed.

Rectified Spirit is the most concentrated alcohol obtainable by distillation. The U. S. Pharmacopœia, under **Alcohol**, U. S. P., calls for a spirit containing 91 per cent. by weight of real alcohol, and of sp. gr. 0.820.

Proof-Spirit has a sp. gr. of 0.9198 at 15.5° C., and according to Fownes contains 49.24 per cent. by weight of alcohol.

Brandy (**Spiritus Vini Gallici**, U. S. P.) is, or should be, the direct product of the distillation of French wines. A great deal of it, however, is factitious, being mixtures of grain-spirit and water to which different coloring and aromatic substances have been added.

Whiskey (**Spiritus Frumenti**, U. S. P.) is the spirit obtained from the fermented wort of corn, rye, and barley, either raw or malted.

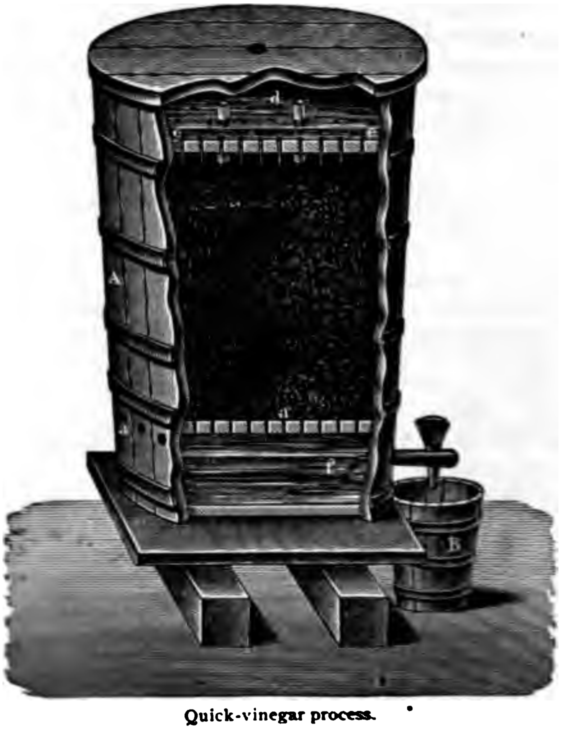
Rum is a spirit obtained in the West Indies from the molasses of the sugar-cane by fermentation and distillation.

Gin is common grain-spirit distilled and aromatized with juniper berries.

4. The Manufacture of Acetic Acid and Vinegars.—The acetic ferment, as before stated, requires for its growth the presence of oxygen. When the germs coming from the air drop into a fermenting or sugary liquid which is suited for their growth they develop rapidly over the surface of the liquid and form a gelatinous skin, which thickens and falls to the bottom of the vessel because of its increasing weight. Another skin forms at once again, and this in turn is replaced by a third, and so on until the liquid is exhausted of assimilable material. This skin, called the "mother of vinegar," consists of a multitude of minute fissure ferments. The raw materials furnishing vinegar under the influence of the acetic fermentation are, first, wine; second, spirits; third, malt wort or beer; fourth, fermented fruit juices other than wine; and fifth, sugar-beets. The wines used are those of inferior vintages and such as are unfit for drinking as wine. They should not exceed 10 per cent. in alcoholic strength. The spirits used for vinegar-making must be so diluted with water and vinegar already formed that the alcoholic strength ranges between 3 and 10 per cent. The malt wort used for malt vinegar is completely fermented and then passed through a filter of wood chips into the acetifier. Cider from apples and perry from pears are about the only fruit juices besides wine fermented for the production of vinegar. Sugar-beets are used somewhat in France for vinegar-making.

Three vinegar-making processes are in use with some special modifications. First, the Orleans process, in which a series of mother-casks or [illegible] holding from fifty to one hundred gallons are used. These [illegible] filled with hot vinegar, and the wine is added in successive [illegible] and corresponding portions siphoned off into storage-vats at in[illegible]. The wine vinegars obtained in this way have an agreeable aroma,

FIG. 102.



Quick-vinegar process.

that made from white wines being the most esteemed. The second process is the so-called "quick-vinegar process." It is used in Germany and this country for spirit vinegar, and in England for malt vinegar. The vinegar-former is shown in Fig. 102. About a foot above the true bottom of the cask it has a false bottom perforated, as shown in the illustration. The space between the false bottom and a wooden disk set in near the top is filled with beech-wood shavings. Just under the false bottom a series of holes is bored in the side of the cask extending all the way around. The shavings are first boiled in water and dried, then soured or soaked in warm vinegar for twenty-four hours before being put in the cask. Air circulates through the space filled with the beech shavings, entering through the holes below, and escaping through the glass tubes in the wooden disk above. The weak alcoholic liquid is then allowed to slowly trickle down through the shavings. The third process is Pasteur's process, using the vinegar fungus, or "mother of vinegar" directly, and causing it to propagate in a liquid containing suitable food (phosphates of potassium, magnesium, and lime).

Cider vinegar, as is well known, is the result of a spontaneous acetification. The different vinegars may contain from 3½ to 6 or even 8 per per cent. of acetic acid. The other constituents vary with the different kinds of materials used in the vinegar formation.

Factitious vinegars are often made from pyroligneous acid flavored with acetic ether and colored with caramel color.

XI. DERIVATIVES OF CARBONIC ACID.

Carbonic acid, $CO(OH)_2$, is not known in the free state, but is supposed to exist in aqueous solution in water charged with CO_2. Both this anhydride and the metallic salts of carbonic acid have already been discussed under Inorganic Chemistry, but a number of organic compounds may properly be considered as derivatives of it, and will be mentioned.

1. Sulphur Derivatives of Carbonic Acid.—From the anhydride carbon dioxide we have, by replacement with sulphur, two derivatives:

Carbon Oxysulphide, COS, is formed when a mixture of sulphur vapor and carbon monoxide is led through a red-hot tube, $CO + S = COS$; also by heating together urea and carbon disulphide, according to the reaction: $CO(NH_2)_2 + CS_2 = COS + NH_4CNS$.

Very inflammable gas, of peculiar odor, burning with blue flame.

Carbon Disulphide, CS_2 (Carbonei Disulphidum, U. S. P.), is formed by heating carbon in sulphur vapor. When pure, has but slight odor, and is a colorless, highly refractive liquid. After exposure to the light it takes a yellow color from liberation of sulphur, and develops an offensive odor. Boils at 47°, solidifies at −116°, and melts again at −110°. Easily soluble in alcohol, ether, chloroform, benzene, fixed and volatile oils; insoluble in water. Sp. gr. 1.268. Inflammable, burning with bluish flame. Is used for dissolving caoutchouc and for the extraction of fats and fatty oils from oil seeds and from bones and wool.

Three thio-carbonic acids are possible, $CS\left\{\begin{matrix}SH\\SH\end{matrix}\right.$, $CO\left\{\begin{matrix}SH\\SH\end{matrix}\right.$ and $CS\left\{\begin{matrix}SH\\OH\end{matrix}\right.$. Of these, it is only necessary to consider the last derivatives of which possess some importance. The ethyl derivative of this acid is called

Xanthogenic Acid, $CS\left\{\begin{matrix}SH\\OC_2H_5\end{matrix}\right.$.—The potassium salt of this acid is formed when carbon disulphide is added to alcoholic potash solution. This salt, $CS\left\{\begin{matrix}SK\\OC_2H_5\end{matrix}\right.$, is used extensively as an antidote for the *phylloxera* insect in the diseases of grape-vines and in the manufacture of artificial indigo. The copper salt, known also as "cuprous xanthate," is a yellow, insoluble compound, the formation of which serves as a characteristic test for carbon disulphide.

2. **Esters of Carbonic Acid.**—Both the neutral ester, $CO(OC_2H_5)_2$, known as ethyl carbonate, and the acid ester, $CO\left\{\begin{matrix}OH\\OC_2H_5\end{matrix}\right.$, known as ethyl-carbonic acid, are known. The former is a neutral liquid of agreeable odor, lighter than water, and insoluble in the latter. Boils at 126°. The latter is the counterpart of ethyl-sulphuric (sulphovinic) acid, and is not known in the free state, but only in its salts.

3. **Chlorides of Carbonic Acid.**—From the anhydride carbon dioxide we have the derivative *carbon oxychloride*, $COCl_2$. It is obtained by the direct combination of carbon monoxide and chlorine in sunlight, and also by the oxidation of chloroform by means of chromic acid. It is a colorless gas (known also as phosgene gas), condensing to a liquid below 8°, and of powerful suffocating odor. It is employed in the preparation of salicylic acid from benzene.

Chloro-carbonic Acid, $COCl(OH)$, is the acid chloride of carbonic acid. Both the free acid and the metallic salts are unstable, and cannot be obtained. Its esters, however, can be prepared, as $COCl(OC_2H_5)$, which is obtained by the action of phosgene gas upon absolute alcohol.

crystalline compounds with both bases and acids, as well as with salts.

Urea is recognized by several characteristic tests. The addition of mercuric nitrate to dilute solutions containing urea causes a white precipitate of a urea-mercuric nitrate compound; if urea crystals be touched with a drop of a concentrated aqueous solution of furfurol, and then a drop of strong hydrochloric acid, a violet color passing into purplish-violet is produced.

Urea may be determined quantitatively when in solution in several ways. First, by the aid of a standard solution of mercuric nitrate (*1* c.c of which corresponds to 0.01 gm. urea). To a measured volume of the urea solution the mercuric nitrate solution is added until all the urea has been precipitated as the double salt ($2CN_2H_4O,Hg(NO_3)_2,3HgO$) and a slight excess of mercury is in the solution. This is recognized by addition of a drop of caustic soda, which gives a yellow precipitate when the mercury is in excess, but a white one as long as urea is present in the solution. This is known as Liebig's method. Second, to the urea solution (urine) is added sodium hypobromite, and the nitrogen evolved is collected in a suitable apparatus and measured. The reaction is: $CON_2H_4 + 3NaOBr = N_2 + Na_2CO_3 + NaBr + 2HBr + H_2O$. This is known as Hüfner's method.

Biuret, $C_2H_5N_3O_2$, results when urea is heated to 150°–170°, ammonia splitting off. Forms long needles, fusing at 190°. When it is dissolved in caustic soda and a little cupric sulphate is added, an onion-red to violet color is obtained, known as the "biuret reaction." This reaction is also given by peptones and by albuminoids after boiling with alkalies.

Thio-urea (Sulphurea), $CS\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$, is formed from ammonium sulphocyanate by prolonged fusion, a molecular rearrangement taking place, $CNS.NH_4 = CS(NH_2)_2$. Heavy rhombic prisms, melting at 172°.

A derivative of sulphurea has been introduced into medicine under the name of *Thiosinamine* (Allyl-sulphurea), $CS\left\{\begin{matrix}NH_2\\NH.C_3H_5\end{matrix}\right.$. It is prepared by the action of ammonia upon mustard oil (allyl sulphocyanate). Colorless or slightly yellowish crystals, fusing at 74°, with slight odor of leeks, easily soluble in water, alcohol, and ether.

Sucrol (or Dulcin), $CO\left\{\begin{matrix}NH_2\\NH.C_6H_4OC_2H_5\end{matrix}\right.$.—This is urea in which a hydrogen atom is replaced by the *p-phenetol* radical (see Aromatic Compounds). This compound has been brought for-d in medicine as a substitute for "saccharin," to be used for

Alloxan (Mesoxalyl-urea), $C_4H_2N_2O_4$, results from the oxidation of uric acid with nitric acid. On further oxidation yields parabanic oxide and carbon dioxide. Decomposes on boiling with alkalies into mesoxalic acid and urea. Alloxan colors the skin purplish-red and imparts to it an unpleasant odor. By reduction with the aid of H_2S it is changed into *Alloxantin*, $C_8H_4N_4O_7$. This attracts oxygen from the air and changes into *Murexide* (Ammonium Purpurate), $C_8H_4(NH_4)N_5O_6$.

Alloxantic Acid (Mesoxaluric Acid), $C_4H_4N_2O_5$, is formed from alloxan by boiling with baryta water. Decomposes on boiling into mesoxalic acid and urea.

Of the Diureïdes, or compounds formed from two molecules of urea, the most important is *Uric Acid*, $C_5H_4N_4O_3$. It is found in urine. The urine of a healthy man contains daily from 0.4 to 0.8 gm. of uric acid. It is, however, especially to be found in the excrements of birds and reptiles, which often consist largely of uric acid and alkaline urates. It is wanting in normal blood, but may be present here under pathological conditions. Gouty concretions and urinary calculi are composed in part of urates. It is usually extracted from the excrement of serpents or guano by the aid of caustic soda, and the free uric acid precipitated from the filtered solution on addition of hydrochloric acid. Insoluble in cold water; difficultly soluble in hot water; insoluble in alcohol and ether. It is soluble in hot solutions of sodium phosphate and acetate, in concentrated sulphuric acid, and in glycerin. A hot, aqueous solution of lithium carbonate also dissolves it abundantly.

Salts of Uric Acid.—Uric acid is a weak, dibasic acid, and forms difficultly soluble salts. *Acid ammonium urate*, $C_5H_3(NH_4)N_4O_3$, is found frequently in calculi from the bladder and kidneys, in the urine of birds and amphibia, and in human urine as a sediment after fermentation begins. *Acid sodium urate* is a chief constituent of the excrement of serpents. It is also found as a sediment in urine, and is recognized by its brick-red color. *Acid potassium urate* is also found in urinary sediment. The most characteristic test for the recognition of uric acid is the *murexide test*. The substance is evaporated with a little nitric acid, leaving a yellowish or reddish residue. After cooling, this is moistened with a little ammonia, when the purplish-red color of murexide (acid ammonium purpurate) is developed. A drop of potassium or sodium hydrate changes this color to the blue color of the potassium or sodium purpurate.

Carnine is supposed to be dimethyl-uric acid, $C_5H_2(CH_3)_2N_4O_3$. It is found to the amount of 1 per cent. in Liebig's extract of meat.

Small amounts of it are also said to be formed when albumen is oxidized with potassium permanganate. Readily deliquescing crystalline mass, absorbing carbon dioxide from the air.

By the replacement of hydrogen atoms in guanidine by acid radicals we obtain derivatives analogous to the ureïdes derived from urea.

Glycocyamine (Guanidine-acetic Acid), $C_3H_7N_3O_2$.—Results from the addition of cyanamide to glycocoll, or from guanidine carbonate and glycocoll.

Creatine (Methyl-glycocyamine), $C_4H_9N_3O_2$, is found in the muscular juice of many animals, even invertebrates, in the blood, and in serous fluids. It may be formed also by the addition of cyanamide to sarcosine (methyl-glycocoll). Is chiefly obtained from extract of meat.

Creatinine (Anhydride of Creatine), $C_4H_7N_3O$, is formed by boiling creatine with acids. Is found also in the urine. It combines with acids and salts. A characteristic compound is that formed with chloride of zinc, difficultly soluble in water, almost insoluble in alcohol.

XII. CYANOGEN AND ITS DERIVATIVES.

The cynogen compounds contain the monad radical $(CN)^I$. The free molecule of cyanogen, like the molecule of chlorine, must be double this atomic group.

Cyanogen, $\begin{array}{c}CN\\|\\CN\end{array}$ or $(CN)_2$, is found free in the gases of blast-furnaces, and is formed when the electric spark is passed between carbon points in an atmosphere of nitrogen. May be conveniently prepared by heating oxalate of ammonium : $C_2O_4(NH_4)_2 = (CN)_2 + 4H_2O$, or by heating mercuric cyanide.

Colorless gas, with peculiar penetrating odor resembling bitter almonds. Very poisonous. It burns with a peach-red color. Is soluble in water and alcohol. These solutions become dark on standing, with separation of a brown powder known as azulmic acid, while oxalic acid, ammonia, formic and hydrocyanic acids, and urea are found in the liquid.

Paracyanogen $(CN)_x$, is a polymer of cyanogen, and is formed as a by-product when cyanogen is made from mercuric cyanide.

1. **Hydrogen Cyanide and other Cyanides.**—The union of the radical CN with hydrogen gives us a compound, HCN, analogous to HCl or HBr in its general chemical relations.

nickel, etc., break up with separation of the insoluble cyanide and liberation of hydrogen cyanide; the other class do not liberate HCN, but a complex acid, in which the CN group is combined with hydrogen and the heavy metal. Thus, $K_4Fe(CN)_6$ is potassium ferrocyanide, and on addition of dilute acid liberates $H_4Fe(CN)_6$, called hydrogen ferrocyanide, and $K_3Fe(CN)_6$, which may be taken as the equivalent of the formula of potassium ferricyanide, on addition of dilute acid liberates $H_3Fe(CN)_6$, called hydrogen ferricyanide. Similar double cyanides with the metal remaining as an integral part of the free acid are formed with manganese and cobalt.

Potassium Ferrocyanide (Yellow Prussiate of Potash), $K_4Fe(CN)_6 + 3H_2O$ (**Potassii Ferrocyanidum,** U. S. P.), is made on a large scale by fusing animal scrap, like horns and hoofs of cattle, blood, leather, etc., with potashes, and adding metallic iron. The fused mass is lixiviated with water, filtered, and crystallized. The reactions which take place may be expressed thus:

$$4C + 2N + K_2CO_3 = 2KCN + 3CO.$$
$$6KCN + FeS = K_4Fe(CN)_6 + K_2S.$$

It forms yellow crystals of the tetragonal system, easily soluble in water, insoluble in alcohol. It is not poisonous. Oxidizing agents like chlorine convert it when in solution into ferricyanide of potassium. With ferric salts it yields an insoluble blue compound, ferric ferrocyanide, known as "Prussian blue," $Fe_4(Fe(CN)_6)_3$. Other insoluble ferrocyanides are those of copper, which is brown, and zinc, which is white. Yellow prussiate of potassium is used technically in the manufacture of Prussian blue, of potassium cyanide, and of hydrogen cyanide.

Potassium Ferricyanide (Red Prussiate of Potash), $K_6Fe_2(CN)_{12}$, is produced by oxidizing the ferrocyanide in solution. Forms red, rhombic crystals, readily soluble in water. The solution gradually decomposes in the light with the formation of the yellow prussiate. In the presence of free alkali it has an oxidizing action, and is changed thereby into the yellow prussiate. With ferrous salts forms a blue precipitate, ferrous ferricyanide (Turnbull's blue).

By the action of nitric acid upon ferrocyanides are formed nitroprussides.

Sodium Nitroprusside, $Na_2Fe(CN)_5(NO) + 2H_2O$, crystallizes in red prisms, readily soluble in water. Serves as a delicate test for soluble sulphides even in dilute solution, giving a fine but transient purplish color.

The cyanides in which an alcohol radical replaces the hydrogen of HCN form two series isomeric with each other known as the *Nitriles* and the *Isonitriles*. This isomerism is explained by the assumption that in the nitriles the atoms in the CN group are linked in one way, $N\equiv C-$, and in the isonitriles they are linked in another way, C≣N—, the nitrogen being triad in the one class and pentad in the other. To the first class belong methyl cyanide or acetonitrile, $CH_3.CN$, ethyl cyanide or propionitrile, C_2H_5CN, etc. These form an homologous series, it is seen, with HCN, which might be called formonitrile. They are all poisonous liquids.

A nitro product of methyl cyanide is the very unstable *fulminic acid*, $CH_2(NO_2).CN$, the mercury salt of which is obtained when a solution of mercuric nitrate reacts with alcohol, and is known as *fulminate of mercury*. This is also explosive, and is used for percussion caps and for fuses to explode dynamite cartridges.

The Isocyanides or Isonitriles differ in many respects from the corresponding cyanides. They are liquids of extremely sickening odor, but are *not* poisonous like the cyanides. They are sometimes called *carbylamines*, as $CH_3.NC$, methyl isocyanide, or methyl carbylamine. The production of one of this class, phenyl carbylamine, when chloroform is heated with aniline and alcoholic potash, was given as a test under Chloroform (see p. 569).

2. Cyanic and Cyanuric Acids.—By the replacement of an H atom in HCN by the group OH we obtain CN.OH. This compound is not known in the free state, but only in its esters. The isomeric compound, CO.NH, however, is known as *Isocyanic Acid*, a very unstable, volatile liquid, which readily polymerizes, and yields Cyanuric Acid, $(CONH)_3$, and *Cyamelide*, $(CONH)_x$.

Potassium Isocyanate (commonly called Cyanate), CONK, is obtained by fusing potassium cyanide or yellow prussiate of potash with metallic lead or manganese peroxide. Forms white scales, easily soluble in water and alcohol.

Ammonium Isocyanate (commonly called Cyanate), $CON.NH_4$, is a white, crystalline mass, which changes on heating into the isomeric compound urea, $CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$. (See p. 663.)

3. Sulphocyanic and Isosulphocyanic Acids.—Corresponding to cyanic and isocyanic acids are the sulphur compounds

$N \equiv C—SH$, sulphocyanic acid, and $CS.NH$, isosulphocyanic acid. The metallic salts are derivatives of the first of these.

Potassium Sulphocyanate, $CNSK$, is readily obtained by fusing ferrocyanide of potassium with sulphur and potash. Colorless, deliquescent prisms, soluble in water, with considerable lowering of temperature.

Ammonium Sulphocyanate, $CN.SNH_4$, is obtained by the action of carbon disulphide upon concentrated ammonia in alkaline solution. Colorless, deliquescent prisms, easily soluble in water. These sulphocyanates are used as reagents to distinguish ferric from ferrous solutions, giving with the former blood-red coloration, while remaining colorless with the latter.

Mercuric Sulphocyanide, $(CN.S)_2Hg$, is a white, insoluble powder. When heated, swells up enormously as it is decomposed. Used in toys known as "Pharaoh's serpents."

Of the esters two series are known, the Sulphocyanates and the Isosulphocyanates. To the first class belong *Ethyl Sulphocyanate*, $CN.SC_2H_5$, and *Allyl Sulphocyanate*, $CN.SC_3H_5$. This latter is the starting-point in the manufacture of artificial mustard oil. By the action of allyl iodide on an alcoholic solution of potassium sulphocyanate this sulphocyanate of allyl is made. It is then distilled, when, by molecular rearrangement, it becomes *Allyl Isosulphocyanate*, $CS.NC_3H_5$, or true mustard oil (**Oleum Sinapis Volatile**, U. S. P.). It is also obtained from the seeds of the black mustard by distillation with water. It forms a liquid slightly soluble in water, of irritating odor, inciting to tears and producing blisters upon the skin. Boils at 151°.

The esters of isosulphocyanic acid are often known collectively as "mustard oils." Thus, we have *methyl-mustard oil*, $CS.NCH_3$; *ethyl-mustard oil*, $CS.NC_2H_5$; *n-propyl-mustard oil*, $CS.NC_3H_7$.

4. **Amides of Cyanogen.**—The only important compound in this series is *Cyanamide*, $CN.NH_2$. May be formed by the action of ammonia upon cyanogen chloride in ethereal solution. Colorless, deliquescent crystals, easily soluble in water, alcohol, and ether. By the action of dilute acids it takes up the elements of water and becomes urea: $CN.NH_2 + H_2O = CO \left\{ \begin{matrix} NH_2 \\ NH_2 \end{matrix} \right.$, and in analogous manner it takes up H_2S and becomes sulphurea, $CS \left\{ \begin{matrix} NN_2 \\ NH_2 \end{matrix} \right.$. When heated with ammonia salts it yields salts of guanidine (see p. 667).

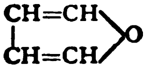
CHAPTER IV.

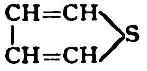
CLOSED-CHAIN GROUPS WITH LESS THAN SIX CARBON ATOMS.

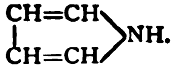
THE compounds thus far considered were all derivatives of methane and the similar hydrocarbons, which, whether saturated or unsaturated, had the one feature in common, that they were *open-chain* hydrocarbons; that is, aggregates of carbon atoms linked together in such a way that the end carbon atoms were distinguished from those occupying a middle position in the molecular grouping.

For benzene and the so-called "aromatic compounds," on the other hand, we must assume that the molecule contains six carbon atoms linked together in a closed chain, so that no one of the six is an end carbon atom. The presumptions in favor of this theory will be stated in the next chapter. As transition compounds from the open-chain compounds to the true aromatic compounds or benzene derivatives may be noted three compounds which show a closed-chain structure in which less than six carbon atoms are present. These are *Furfurane* (or *Furane*), C_4H_4O, *Thiophene*, C_4H_4S, and *Pyrrol*, C_4H_4NH. Of these, the first is most nearly related to the methane derivatives, being formed in many cases in the decomposition of the sugars and carbohydrates, and the other two accompany benzene in the products of destructive distillation, and more nearly resemble the true aromatic compounds. The structural formulas given to the three compounds show a close similarity and relationship, and the fact that all three may be derived from the same compounds by three different reactions goes to establish this relationship.

The formulas ascribed to them are:


Furfurane.


Thiophene.


Pyrrol.

All three are liquids, boiling at relatively low temperatures,—furfurane at 32°, thiophene at 84°, and pyrrol at 130°.

All three are insoluble, or only slightly soluble, in water, but easily soluble in alcohol and ether. They show analogous color reactions. All three give blue or violet coloring matters with isatin and sulphuric acid ; the vapor of pyrrol colors a pine shaving that has been moistened with HCl carmine-red (whence the name, from πυρρός, fiery-red), while furfurol vapor colors it an emerald-green.

All three are derived from mucic acid by different reactions. Mucic acid destructively distilled yields first pyromucic acid (furfurane-carboxylic acid), $C_4H_3O(COOH)$, and this on further heating splits off CO_2, and yields furfurane ; by the dry distillation of ammonium pyromucate is obtained pyrrol ; and by the action of hydrogen sulphide upon pyromucic acid is formed thiophene.

Similarly all three are derived from acetonyl-acetone by different reactions, and both pyrrol and thiophene from succinic acid by the action of different reagents.

1. Furfurane and its Derivatives.—*Furfurane* (or *Furane*), C_4H_4O, is formed by the distillation of pine wood. Is a colorless, mobile liquid of chloroform-like odor, boiling at 32°. It is recognized by the emerald-green color which it imparts to a pine shaving which has been moistened with hydrochloric acid. Besides furfurane, methyl-furfurane appears to be present also in pine-wood tar.

Furfurol (Furfurane Aldehyde), $C_4H_3O.COH$, results from the oxidation of the sugars with manganese dioxide and sulphuric acid, as well as from the distillation of the pentoses, bran, sawdust, starch, gum arabic, etc., with sulphuric acid. It is contained in beer and in fusel oil, and hence in brandy. It is also decomposition product of the albuminoids. It is a colorless oil of agreeable odor, resembling that of bitter almonds, turning brown in the air. As an aldehyde it reduces ammoniacal silver solution.

Pyromucic Acid, $C_4H_3O.COOH$, is the acid corresponding, and is produced by the oxidation of furfurol as well as in the dry distillation of mucic acid. Needles or plates, melting at 134°, resembling benzoic acid in appearance.

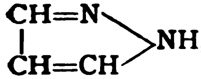
2. Thiophene and its Derivatives.—*Thiophene*, C_4H_4S, accompanies benzene, C_6H_6, in coal-tar, and is only separated from it with difficulty. Its homologues likewise accompany those of benzene, displaying nearly the same boiling points and many similar reactions. It is separated from the crude benzene of coal-tar by shaking out with successive quantities of concentrated sulphuric acid, in which it is soluble. Is a liquid of weak odor, boiling at 84°. The most delicate test for it is the blue color due to the formation of indophenin, obtained on shaking a solution containing it with sulphuric acid and isatin.

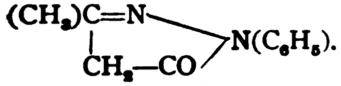
Two thiophene derivatives have been recommended for use in medicine :

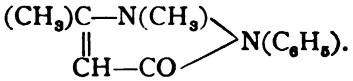
Thiophene Diiodide, $C_4H_2I_2S$, and *Sodium Thiophene-sulphonate*, $C_4H_3S.SO_3Na$.—The former, which is recommended as a substitute for iodoform, is in colorless, readily volatile crystals, melting at 40.5° C. The odor is aromatic but not unpleasant. It is insoluble in water, but easily soluble in ether, chloroform, and in hot alcohol. It contains 75.5 per cent. of iodine and 9.5 per cent. of sulphur. The second compound is a white, crystalline powder, recommended for use in salve in cases of prurigo.

3. Pyrrol and its Derivatives.—*Pyrrol*, C_4H_4NH, is obtained in the dry distillation of bones and in coal-tar. It is a liquid, boiling at 130°, and smelling like chloroform. Is insoluble in water and alkalies, soluble in alcohol, ether, and dilute acids.

Tetraiodopyrrol (*Iodol*), C_4I_4NH.—When iodine in alcoholic solution acts upon pyrrol, especially in the presence of an alkali, a substitution compound, to which the name of iodol has been given, separates out in a yellow, crystalline powder, insoluble in water, soluble in alcohol. It is used as an odorless substitute for iodoform, and is especially characterized by its high percentage of iodine (88.97 per cent.).

Antipyrin (*Phenyl-dimethyl-pyrazolon*), $C_{11}H_{12}N_2O$.—By the action of phenyl-hydrazine, $C_6H_5.NH.NH_2$, upon aceto-acetic ether (see p. 614) water and a molecule of alcohol are split off, and a compound is obtained which is called phenyl-methyl-pyrazolon. This would be a derivative of the yet unknown pyrazol,


, a compound differing from pyrrol only in the substitution of the nitrogen atom for the triad group CH. In the phenyl-methyl-pyrazolon we would have besides the substitution of the radicals phenyl and methyl the change of a CH group for the dyad group CO, making its structural formula


. When this is methylated by the action of methyl iodide, there is formed the hydrogen iodide compound of the new base phenyl-dimethyl-pyrazolon, which possesses the structural formula


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The free base comes into commerce as a white, crystalline powder, melting at 113°, almost odorless, easily soluble in water, alcohol, chloroform, difficultly soluble in ether. As a base it forms addition salts with the acids like ammonia. It shows two characteristic color reactions: with ferric chloride it is colored deep red, which color is changed by sulphuric acid into bright yellow; with nitrous acid a green color, and in concentrated solutions a separation of green crystals of isonitroso-antipyrin $C_{11}H_{11}N_3O_2$. Both these reactions are adapted for the recognition of antipyrin in urine. Antipyrin is probably the best known of the newer synthetic remedies.

Antipyrin Salicylate (Salipyrin), $C_{11}H_{12}N_2O.C_7H_6O_3$, forms a colorless, crystalline powder, melting at 92°. Used as an antineuralgic remedy.

Iodo-pyrin (Iodo-antipyrin), $C_{11}H_{11}IN_2O$, forms lustrous, colorless, prismatic needles, difficultly soluble in cold water, more readily in hot water. Melts at 160°.

Naphtho-pyrin (β-naphtol-antipyrin) is a molecular combination of β-naphtol and antipyrin. Recently introduced into medicine.

Monochloral-antipyrin (Hypnal) and *Bichloral-antipyrin* have been mentioned under Chloral-hydrate (see p. 592).

Tolypyrin (Tolyl-dimethyl-pyrazolon), $C_{12}H_{14}N_2O$, is a homologue of antipyrin. Made by using instead of phenyl-hydrazine the homologous compound *p*-tolyl-hydrazine in the reaction with aceto-acetic ether. Colorless crystals, fusing at 136°–137°, soluble in water and alcohol, difficultly soluble in ether. Shows the same color reaction with ferric chloride and nitrous acid as antipyrin.

Tolypyrin Salicylate (Tolysal), $C_{12}H_{14}N_2O.C_7H_6O_3$, is formed by the direct union of the two components. Is in every way analogous to antipyrin salicylate.

CHAPTER V.

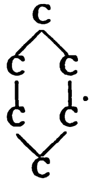
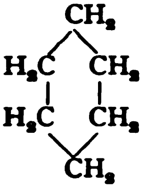
CLOSED-CHAIN OR AROMATIC COMPOUNDS (CYCLIC HYDROCARBONS AND DERIVATIVES).

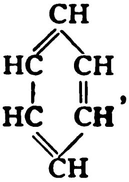
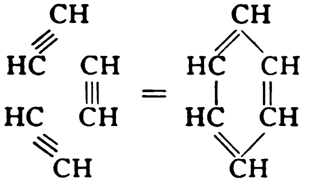
IN studying the methane derivatives we had several series of hydrocarbons, of which that containing the maximum hydrogen in any given case for the amount of carbon present was called the Paraffin series, and had assigned to it the general formula C_nH_{2n+2}. This series was also termed the saturated series of hydrocarbons, because no addition compounds could be formed. The explanation of this fact and the verification of the general formula just stated were both found in the structural formulas, showing an open-chain formation with single linking of adjacent carbon atoms. The other series of hydrocarbons, with the general formulas C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4}, and C_nH_{2n-6}, respectively, were all unsaturated hydrocarbons and ready to unite directly with halogen atoms and atomic groups to form addition compounds. The explanation of this fact was also given in the structural formulas, which showed an open-chain formation, but with double and treble linking between certain of the carbon atoms. This form of linking was seen to be unstable, and hence the tendency to pass into saturated compounds with an open-chain structure and single linking of the carbon atoms.

We meet, however, in the Benzene series of hydrocarbons, which are the products of the distillation of many complex substances, and which are found to be the fundamental substances of an immense number of compounds occurring in the vegetable kingdom, hydrocarbons of the general formula C_nH_{2n-6}, which are relatively stable and more like saturated than unsaturated hydrocarbons. While it is true that addition of halogen atoms may be effected within certain limits, these compounds do not tend to form as readily as substitution compounds, in which the hydrogen atoms of the original hydrocarbons are readily replaced by halogens and radicals like methyl and ethyl.

The fundamental hydrocarbon of this series is benzene, C_6H_6, and the homologues are formed by the replacement of one or more of these six hydrogen atoms by methyl and ethyl groups. The limit of this replacement is reached, of course, when six hydrogen atoms have been exchanged for other atoms or atomic groups. Both the hydrocarbons of this series and the substitution derivatives are more stable than the addition compounds before referred to. Moreover, all the derivatives of benzene can be converted either into benzene itself or into very nearly allied compounds by relatively simple reactions. Benzene is, then, in a peculiar degree both the starting-point and the basis of the compounds connected with it.

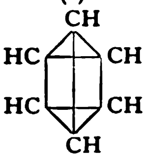
It is obvious, then, that benzene and its homologous hydrocarbons must be differently constituted structurally from the paraffin series or any of the unsaturated series that are convertible into methane derivatives by addition. The benzene derivatives are not convertible into marsh-gas derivatives by addition of halogen or other atomic groups; benzene, C_6H_6, cannot be converted into hexane, C_6H_{14}, by any means, direct or indirect. As stated before, addition compounds can be formed. We can obtain $C_6H_6Cl_6$ and from this C_6H_{12}, but the addition of hydrogen stops there. It is strikingly evident, from this and many similar observations, that C_6H_6 is a peculiarly-constituted molecule, which resists change and remains substantially intact through all the substitutions that may be effected. We cannot transform it into a simpler molecule containing 5, 4, or 3 carbon atoms; when oxidized, which is only accomplished with difficulty, it goes into carbon dioxide and water.

1. Theories as to the Structure of the Benzene Molecule.—The theory as to the constitution of the benzene molecule which has found general acceptance is that of Kekulé, first published in 1866. This not only explains known facts with regard to benzene and its thousands of derivatives, but has found confirmation in the discovery and preparation of the immense numbers of so-called "coal-tar" products which are chemically grouped and classified by its aid. According to this theory the six carbon atoms are linked together in such a way as to form a *closed chain*. We may arrange them in a continuous chain of which the two ends are connected together, but there is no reason here for making it a longitudinal chain. Therefore the six carbon atoms may be considered as placed at equal distances apart on the circumference of a circular ring, or in any other position that might be assumed by a closed chain of six units, but for convenience in writing the hexagon figure is usually chosen. The benzene molecule would then show as its framework . Each of these carbon atoms has attached to it one atom of saturating hydrogen in the formula C_6H_6. If each carbon atom had two hydrogen atoms attached we would have  or C_6H_{12}, and it is obvious that the four bonds of tetrad carbon would be satisfied.

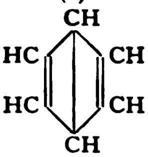
But C_6H_6 is the formula of the stable molecule and not C_6H_{12}. The latter readily gives up six atoms of hydrogen on oxidation. Kekulé, therefore, considers that each carbon atom in the benzene molecule is linked doubly with one other carbon. This would make an alternate single and double linking, as shown in the formula , and chemists have generally adopted this graphic expression for the benzene molecule. This formula agrees very well with the formation of benzene from acetylene, $H—C \equiv C—H$, three molecules of the latter uniting at a low red heat to form one molecule of benzene, or the formation of mesitylene (trimethyl-benzene)  from acetone (see p. 594) when the latter is distilled with dilute sulphuric acid. It also explains the capability of benzene and its derivatives to form addition compounds up to a certain limit. As, however, no experimental proof of this particular structural formula can be given, other formulas have been proposed, such as those of

(1) Claus and Koerner, (2) Dewar, and (3) Ladenburg. None of these, however, explains all the observed reactions of benzene and its derivatives as well as the structural formula originally proposed by Kekulé.

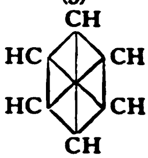
(1)



(2)



(3)



2. Formation of Benzene Homologues.—In the case of open-chain hydrocarbons, whether of the saturated or unsaturated series, the successive homologues were formed by lengthening the chain or adding on additional carbon atoms with the requisite saturating hydrogen. Thus, following methane we had ethane, propane, butane, etc., and following ethylene we had propylene, butylene, etc. In the case of benzene the closed-chain structure precludes this method of forming an homologous series. But we have following benzene, C_6H_6, toluene, C_7H_8, xylene, C_8H_{10}, etc., as far as $C_{12}H_{18}$. A slight examination of these compounds, as, for example, with oxidizing agents, shows that there are two parts in them of very different stability, a *nucleus*, C_6H_5 or C_6H_4, not oxidizable, and one or two *side-groups*, CH_3, which have replaced hydrogen atoms of the original C_6H_6, and are easily oxidized to COOH groups. In other words, toluene is methyl-benzene, xylene is dimethyl-benzene, etc., and their formulas may be written $C_6H_5.CH_3$ and $C_6H_4(CH_3)_2$, etc., up to hexamethyl-benzene, $C_6(CH_3)_6$, when this series of homologues stops. It is true we can have ethyl-benzene and diethyl-benzene or methyl-propyl-benzene and similar derivatives, but these are not found in any great number in nature. Nor are their derivatives of the same importance as those of the methylated benzenes.

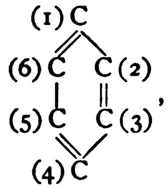
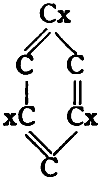
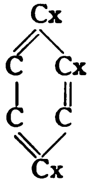
3. Differences between the Benzene Hydrocarbons and the Open-Chain Hydrocarbons.—(*a*) We notice first that the action of concentrated nitric acid is quite different. With the closed-chain hydrocarbons a hydrogen atom of the nucleus is readily replaced by the group NO_2, as $C_6H_6 + NO_2.OH = C_6H_5.NO_2 + H_2O$, the product being called nitrobenzene. With paraffin hydrocarbons nitric acid has little or no action, even when heated for a time.

(*b*) With concentrated sulphuric acid the benzene hydrocarbons give rise to sulphonic acids, as $C_6H_6 + SO_3H.OH = C_6H_5(SO_3H) + H_2O$, the product being called benzene-sulphonic acid. Concentrated sulphuric acid has no action on the paraffin hydrocarbons, and with the olefines it forms addition compounds without displacement of hydrogen.

(*c*) As mentioned before, under the influence of oxidizing agents the homologues of benzene are easily oxidized, yielding the corresponding carboxylic acids. Thus, toluene, $C_6H_5—CH_3$, is oxidized by dilute nitric acid or by chromic acid to benzoic acid, $C_6H_5.COOH$. The open-chain hydrocarbons are only acted upon by oxidizing agents with great difficulty.

(*d*) The hydroxyl derivatives like $C_6H_5.OH$ are quite different from the simple OH derivatives of the paraffin or other open-chain hydrocarbons. The former have more of an acid character, while the latter are basic hydrates. Thus, C_6H_5OH is phenol or carbolic acid, while $C_2H_5.OH$ is ethyl alcohol, which forms esters or salts with the acids.

4. Isomerism in the Closed-Chain Hydrocarbons.—In the hydrocarbons of the paraffin series it is possible to obtain isomeric mono-substitution derivatives, as, for example, normal propyl chloride, $CH_2Cl.CH_2.CH_3$, and isopropyl chloride, $CH_3.CHCl.CH_3$; in the case of benzene, isomeric mono derivatives *cannot* be obtained. The six hydrogen atoms of the benzene seem to possess an equal value. It is a closed-chain structure, and it matters not at what point in the ring thus formed the single substitution takes place. This fact has been proved experimentally. It is different when two atoms of hydrogen in the benzene molecule are replaced by other atoms or groups. These di-substitution derivatives may exist in three isomeric modifications. We may have three dichlor-benzenes, three dimethyl-benzenes, three dinitro-benzenes, etc. This also has been established experimentally, and the limit set at three.

If we now look at the benzene molecule as figured in Kekulé's theory, we see the explanation of this fact. Taking the structural formula , and numbering the carbon atoms from the top going to the right, we have for the purpose of representation each one indicated. Now, if the replacement take place at substitution derivative which would be marked *v*, as *v*-trinitrobenzene, while the figures  and  would be designated by the *s* and *a* respectively, as *s*-trimethyl-benzene and *a*-trichlor-benzene.

These cases of isomerism, it will be noticed, are all concerned with the position in the nucleus assumed by the replacing atom or group. We may also have side-group isomerism, as normal propyl-benzene and isopropyl-benzene.

More important than this last, however, is the case where a substituent enters the benzene nucleus in one case and the side-group in another case, giving us the so-called "mixed isomerism." Thus, $C_6H_4Cl.CH_3$, monochlor-toluene, and $C_6H_5CH_2Cl$, benzyl chloride, or $C_6H_4(CH_3)_2$, xylene, and $C_6H_5.C_2H_5$, ethyl-benzene, are isomeric.

The determination of the nature of a di-substitution derivative of benzene, whether ortho, meta, or para, is to be accomplished by the treatment with reagents, whereby the nature of the side-group may be changed and the product studied as to its properties. Ortho derivatives through a series of such changes will remain ortho derivatives, and so with the meta and the para compounds. By such a series of transformations it becomes possible correctly to identify the nature of the original compound.

CHAPTER VI.

AROMATIC COMPOUNDS CONTAINING ONE NUCLEUS.

In explaining the theories held as to the fundamental differences between the aromatic compounds and the open-chain hydrocarbons and their derivatives, we have touched only upon the structure of benzene, taking it as the type of closed-chain compounds, and, in fact, the starting-point from which they are derived. We will see, however, later, that two or more of these benzene nuclei may unite, either by simple linking without condensation, or by condensing together to form a compound nucleus, obviously related to the simpler benzene molecule, but built up by its doubling or trebling itself. Thus, diphenyl, diphenyl-methane, triphenyl-methane, and indigo all represent aromatic compounds with more than one benzene nucleus in which the parts are linked together without condensation of the nuclei. On the other hand, naphthalene, anthracene, phenanthrene, quinoline, and acridine all represent molecules formed by the condensation of benzene nuclei.

We shall first confine our attention to those aromatic compounds in which a single benzene nucleus appears as the basis of the molecule.

I. HYDROCARBONS.

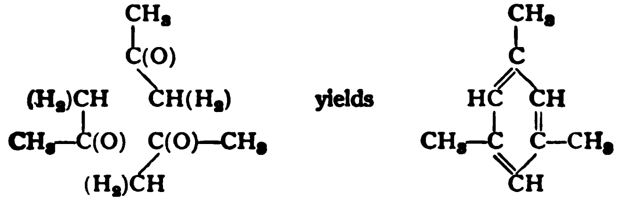
1. Saturated Hydrocarbons.—We have here to deal with benzene and its homologues. They occur to some extent in the free state in nature, being found in Galician and Hanoverian petroleum, and even in small amount in Pennsylvania petroleum. They are obtained, however, most abundantly as the product of the destructive distillation of bituminous coal, and hence are contained in coal-tar. This is a very complex mixture, and more than forty distinct compounds of the aromatic class have been identified in it. When roughly fractioned from the tar-stills it yields three main fractions: (1) The light oil, sp. gr. 0.9, boiling point up to 150°, which contains mainly benzene and its homologues, with some naphthalene; (2) middle oil, sp. gr. up to 1.01, boiling point 150° to 210°, which contains especially naphthalene, carbolic and cresylic acids, and quinoline bases; and (3) heavy oil, sp. gr.

up to 1.04, boiling point from 210° to 300°, containing chiefly anthracene and phenanthrene.

From the first of these fractions, by careful fractionating with the aid of column stills, the benzene hydrocarbons may be obtained. Their separation, however, is not entirely possible by fractional distillation alone, but requires special treatment with reagents.

Benzene derivatives can be formed from bodies of the methane series by a number of reactions, some of which may be noted.

The vapors of alcohol when led through a red-hot tube yield benzene. Acetylene polymerizes at a low red heat, three molecules uniting to form one molecule of benzene. This has been illustrated graphically (see p. 679). Allylene, C_3H_4, in the same way polymerizes to form mesitylene or trimethyl-benzene, C_9H_{12}, when distilled with dilute sulphuric acid. Ketones condense to benzene hydrocarbons when distilled with dilute sulphuric acid. Thus, acetone yields mesitylene:



Hexyl iodide, $C_6H_{13}I$, can be converted into hexachlor-benzene, C_6Cl_6, by heating it with ICl_3, and into hexabrom-benzene, C_6Br_6, by heating the hexyl iodide with bromine at 260°.

Mellitic acid, $C_6(COOH)_6$, is produced by the oxidation of graphite or lignite by means of potassium permanganate.

Potassium carboxide, $C_6(OK)_6$, which is formed by the action of carbon monoxide upon potassium, is the potassium compound of hexoxy-benzene, $C_6(OH)_6$.

These methods, however, may be said to be isolated reactions, and not used as general methods for their production. Among the general methods may be mentioned:

1. By treating a mixture of brominated hydrocarbon and methyl or ethyl iodide with sodium in ethereal solution: $C_6H_5Br + CH_3I + Na_2 = C_6H_5.CH_3 + NaI + NaBr$.

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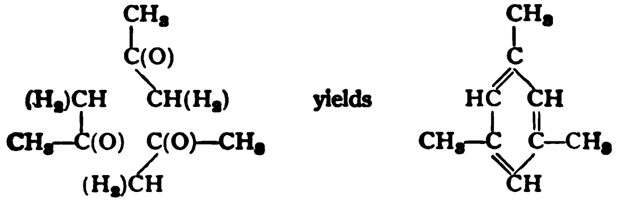

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BENZENE SERIES, SATURATED HYDROCARBONS. GENERAL FORMULA, C_nH_{2n-6}.

C_6H_6	C_6H_6, Benzene, boiling point 79°.			
C_7H_8	$C_6H_5.CH_3$, Toluene, boiling point 111°.			
C_8H_{10}	$C_6H_4(CH_3)_2$, Xylenes : *o*- b. p. 142°, *m*- b. p. 137°, *p*- b. p. 137°.	$C_6H_5(C_2H_5)$, Ethyl-benzene, boiling point 134°.		
C_9H_{12}	$C_6H_3(CH_3)_3$, Trimethyl-benzenes: *s*- = Mesitylene, b. p. 163°. *a*- = Pseudo-cumene, b. p. 169°. *v*- = Hemellithene, b. p. 175°.	$C_6H_4(CH_3)(C_2H_5)$, Methyl-ethyl-benzenes, or Ethyl-toluenes : *o*- b. p. 160°, *m*- b. p. 159°, *p*- b. p. 162°.	$C_6H_5(C_3H_7)$, Normal propyl-benzene, b. p. 157°. Isopropyl-benzene (cumene), b. p. 153°.	
$C_{10}H_{14}$	$C_6H_2(CH_3)_4$, Tetramethyl-benzenes : *s*- = Durene, m. p. 79°, b. p. 190°. *a*- = Isodurene, b. p. 195°. *v*- = Prehnitene, m. p. —4°, b. p. 204°.	$C_6H_3(CH_3)_2(C_2H_5)$, Dimethyl-ethyl-benzenes. Six isomers possible.	$C_6H_4(C_2H_5)_2$. Diethyl-benzenes (3). $C_6H_4(CH_3)(C_3H_7)$. Cymene, b. p. 176°. Six isomers possible.	$C_6H_5(C_4H_9)$, Butyl-benzenes. Four isomers possible.
$C_{11}H_{16}$	$C_6H(CH_3)_5$, Pentamethyl-benzene, m. p. 51°, b. p. 231. $C_6H_5(C_5H_{11})$, Amyl-benzene, etc.			
$C_{12}H_{18}$	$C_6(CH_3)_6$, Hexamethyl-benzene, m. p. 164°, b. p. 264. $C_6H_3(C_2H_5)_3$, Triethyl-benzene, etc.			

3. The benzene hydrocarbons result from their respective carboxylic acids by distilling them with soda-lime : $C_6H_5.COOH = C_6H_6 + CO_2$.

4. From sulphonic acids by the separation of the SO_3H group: $C_6H_4(CH_3)SO_3H + H_2O = C_6H_5(CH_3) + H_2SO_4$.

5. By distillation of the phenols with zinc-dust.

The general characters of the benzene hydrocarbons that seem most important are:

1. They may all be distilled without decomposition. Most of them are colorless liquids of peculiar aromatic odor. Durene, penta- and hexamethyl-benzene are crystalline solids at ordinary temperatures.

2. As before stated, they readily form nitro and sulphonic derivatives.

3. Benzene oxidizes with some difficulty to oxalic, formic, and carbonic acids ; the aromatic hydrocarbons with side-groups are readily oxidized to acids, as $C_6H_4(CH_3)_2 = C_6H_4(COOH)_2$.

4. By reduction with hydrogen iodide under pressure at high temperatures the benzene hydrocarbons add on hydrogen up to the limit of six atoms.

5. The halogens form with benzene in sunlight addition compounds like $C_6H_6Cl_6$. On the other hand, in diffused daylight they form substitution compounds like C_6H_5Cl.

The most important of the benzene hydrocarbons are shown arranged in tabular form on the next page.

Benzene, C_6H_6, was discovered by Faraday in 1825, and detected in coal-tar by Hofmann in 1845. It is practically always obtained from the light oil of tar by taking the purified fraction boiling at 83°–85° and chilling it, when the benzene will crystallize out from the adhering portions of higher homologues. It is also obtainable from illuminating gas, or perfectly pure by distilling benzoic acid with lime. It has a melting point of +4°, and a boiling point of 80.5°. Sp. gr. at 0° 0.9. It burns with a luminous but smoky flame. It is an excellent solvent for fats, resins, iodine, sulphur, and phosphorus. Commercial benzene generally contains thiophene, and hence gives the indophenin reaction (see p. 675). Is used on a large scale as the starting-point for the manufacture of aniline and other technical products of value in the color industry.

Toluene (Methyl-benzene), $C_6H_5.CH_3$, is formed by the distillation of certain resins, as Tolu balsam (whence the name), dragon's-blood, etc. Is generally obtained along with benzene

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giving rise to a great number of isomers. The halogen atoms which are attached to the nucleus are much more firmly held than those which enter in the side-group only. Ammonia and oxidizing agents will attack and eliminate the chlorine of the side-group, but not affect that contained in the nucleus. This action of oxidizing agents is so distinctly different as to serve to distinguish whether the chlorine is present in the one position or the other.

SUMMARY OF HALOID SUBSTITUTION PRODUCTS.

C_6H_5Cl, Chloro-benzene, b. p. 133°.	C_6H_5Br, Bromo-benzene, b. p. 154°.	C_6H_5I, Iodo-benzene, b. p. 185°.
$C_6H_4Cl_2$, Dichloro-benzenes. *o*- 179°, *m*- 172°, *p*- 173°.	$C_6H_4Br_2$, Dibromo-benzenes. *o*- 224°, *m*- 219°, *p*-219°.	Diiodo-benzenes.

$C_6H_3Cl_3$, Trichloro-benzenes, three isomers.
$C_6H_2Cl_4$, Tetrachloro-benzenes, three isomers.
C_6HCl_5, Pentachloro-benzene.
C_6Cl_6, Hexachloro-benzene, m. p. 226°, b. p. 332°.

$C_6H_4Cl(CH_3)$	Isomeric with	$C_6H_5.CH_2Cl$.
Chloro-toluenes, three isomers.	" "	Benzyl chloride, b. p. 179°
$C_6H_3Cl_2(CH_3)$	" '	$C_6H_5.CHCl_2$.
Dichloro-toluenes, six isomers .	" "	Benzal chloride, b. p. 206°.
—— ——		Benzo-trichloride, b. p. 213°.
—— ——		$C_6H_5.CCl_3$.
$C_6H_3Cl(CH_3)_2$	" "	$C_6H_4(CH_3)CH_2Cl$.
Chloro-xylenes, six isomers .	" "	Xylyl chlorides.

Modes of Formation.—Chlorine and bromine acting upon benzene readily yield monochloro- and monobromo-benzene. A further substitution takes place especially easily in the presence of iodine. This acts as a carrier of chlorine or bromine, and by its presence aids in the introduction of these elements.

In the homologues of benzene, if the chlorination takes place in the cold, the chlorine enters the nucleus; if at a boiling temperature, it enters the side-group.

The action of phosphorus pentachlorides upon phenols and aromatic alcohols also serves to form the halogen derivatives.

The nitro or primary amido compounds of the benzene hydrocarbons may also be converted into halogen compounds by first converting them into the diazo compounds, and then boiling these with cuprous chloride:

$$C_6H_5.N{=}N.Cl \;=\; C_6H_5Cl \;+\; N_2.$$

Monochloro-benzene, C_6H_5Cl,
Monobromo-benzene, C_6H_5Br,
Monoiodo-benzene, C_6H_5I,
are all colorless liquids of peculiar, aromatic odor. The boiling points have been given in the table.

Benzyl Chloride, $C_6H_5.CH_2Cl$, is formed by the action of chlorine upon toluene at a boiling temperature. When oxidized it yields benzoic acid. This reaction, together with the fact that prolonged boiling with water or potassium carbonate solution changes it into benzyl alcohol, $C_6H_5.CH_2OH$, shows that the chlorine is present in the side-group. Colorless liquid, boiling at 179°. It is used on a large scale for the manufacture of benzoic aldehyde (oil of bitter almonds).

Benzal Chloride, $C_6H_5.CHCl_2$, is produced by the further chlorination of boiling toluene, also from benzoic aldehyde by the action of PCl_5.

It is used in the manufacture of benzaldehyde and benzoic acid. When heated with water or sulphuric acid, or, as is done on a large scale, with water and calcium hydrate, the benzal chloride is changed into the aldehyde, $C_6H_5CHCl_2 + H_2O = C_6H_5.CHO + 2HCl$.

Benzo-trichloride, $C_6H_5.CCl_3$, sometimes termed Phenyl-chloroform, is used on a large scale for the manufacture of artificial benzoic acid. For this purpose it is heated with water under pressure:

$$C_6H_5.CCl_3 \;+\; 2H_2O \;=\; C_6H_5.COOH \;+\; 3HCl.$$

III. SULPHONIC DERIVATIVES.

The sulphonic acids of the aromatic series, like those mentioned under the methane derivatives, contain the monad group HSO_3, but are much more readily formed. They result from the action of strong or fuming sulphuric acid upon a great variety of aromatic compounds, and play quite an important part in the technical application of the benzene derivatives, and latterly in the manufacture of synthetic compounds of medicinal value. Thus we may have the following classes of sulphonic acid derivatives:

1. Sulphonic acids of the hydrocarbons, as benzene-sulphonic acid, $C_6H_5HSO_3$.

2. Sulphonic acids of the phenols, as phenol-sulp $C_6H_4(OH)HSO_3$.

3. Sulphonic acids of the amines, as amido-benzen acid, $C_6H_4(NH_2)HSO_3$.

4. Sulphonic acids of the diazo compounds, as diaz sulphonic acid, $C_6H_4<\substack{SO_3\\N:N}>$.

5. Sulphonic acids of the azo compounds, as azo-b phonic acid, $C_6H_5.N:N-C_6H_4HSO_3$.

6. Sulphonic acids of the hydrazines, as phenyl- sulphonic acid, $C_6H_5.NH-NH-HSO_3$.

In general, these sulphonic acids and their salts are compounds, mostly soluble in water, difficultly soluble

When fused with caustic potash or soda, they yie and sulphites, $C_6H_5.NaSO_3 + NaOH = C_6H_5.OH +$

When distilled with potassium cyanide, they yield nitriles.

When heated with fuming hydrochloric acid or under pressure, they regenerate the same hydrocar which they were originally formed, $C_6H_5.HSO_3 + H$ $+ H_2SO_4$.

Benzene-monosulphonic Acid, $C_6H_5.HSO_3$, is ob heating benzene with concentrated sulphuric acid. of sulphuric acid is removed by addition of barium c bonate, as both the barium and lead salts of the sulp are soluble. It forms small, crystalline leaflets, deliq the air, and easily soluble in water. Because of the above, that when fused with caustic alkalies it yields p of importance in the manufacture of synthetic carboli

Benzene-disulphonic Acids, $C_6H_4(HSO_3)_2$.—Three i obtainable. The para compound when fused with ca yields the diatomic phenol, resorcin. (See Resorcin.)

Toluene-sulphonic Acids, $C_6H_4(CH_3)HSO_3$, exist isomeric modifications.

Xylene-sulphonic Acids, $C_6H_3(CH_3)_2HSO_3$.—The di mers of this substance are utilized to separate the isomer (See p. 688.)

The higher homologues of benzene, except hexam zene, are all capable of yielding sulphonic acids.

The sulphonic acids of the several classes of benze tives will be mentioned, when of sufficient importance, different groups of compounds.

IV. NITRO DERIVATIVES.

By the action of strong nitric acid upon the aromatic hydrocarbons, derivatives in which one or more hydrogen atoms are replaced by the monad group, NO_2, are formed. These are mostly soluble in the strong nitrating acid, and are thrown out of solution on dilution with water. Thus, from benzene we have $C_6H_6 + NO_2.OH = C_6H_5.NO_2 + H_2O$, and from toluene $C_6H_5.CH_3 + NO_2OH = C_6H_4(CH_3)NO_2 + HOH$. When more than one such replacement takes place, we distinguish by the names mononitro-benzene, dinitro-benzene, trinitro-benzene, etc.

In all these cases the NO_2 group attaches itself to the nucleus, and not to the side-group. Whether one or more such replacements shall take place is dependent upon the strength of the acid and the length of time of its action.

The nitro compounds are mostly pale yellowish liquids, distilling undecomposed in a current of steam, or, in the case of the higher derivatives, yellowish needles or prisms. They are heavier than water, and insoluble therein, but generally soluble in alcohol, ether, and glacial acetic acid. All the nitro compounds are reduced in acid solution by the action of nascent hydrogen, forming the corresponding amido compounds. This may be effected by the action of tin and hydrochloric acid, stannous chloride and hydrochloric acid, or iron and acetic acid. Thus, $C_6H_5.NO_2+H_6=C_6H_5.NH_2+2H_2O$ and $C_6H_4(NO_2)_2+H_{12} = C_6H_4(NH_2)_2 + 4H_2O$.

The nitro compounds are of very great technical importance as necessary steps in the manufacture of aniline and similar amido compounds.

Nitro-benzene, $C_6H_5.NO_2$, is formed by adding benzene gradually to well-cooled fuming nitric acid as long as it seems to dissolve. After some standing the nitro-benzene is separated by the addition of water, washed with water and dilute caustic soda, and purified by distilling in a current of steam. It forms a light yellowish liquid smelling strongly of bitter almonds, boiling at 205°, and crystallizing in needles at 3°. It is manufactured on a large scale as a step in the manufacture of aniline, and pharmaceutically, under the name of "mirbane oil," as a basis of toilet preparations, soaps, etc., because of its characteristic odor. It is poisonous.

Dinitro-benzenes, $C_6H_4(NO_2)_2$, are formed when benzene is added to a mixture of equal volumes of concentrated nitric and sulphuric acids and the mixture heated to boiling. All three isomers are solid and crystallizable.

Nitro-toluenes, $C_6H_4(CH_3)NO_2$.—When toluene is acted upon by strong nitric acid, the ortho- and paranitro-toluenes are formed, the meta compound being absent, although obtainable by indirect means. By boiling with fuming nitric acid the nitro-toluenes are changed into dinitro-toluenes.

Commercial benzene, being always a mixture of benzene and toluene, yields on nitration a mixture of nitro-benzene with the several nitro-toluenes above mentioned.

The presence of a halogen atom replacing an atom of hydrogen in the benzene nucleus does not interfere with the nitration, so that compound derivatives are easily formed. Thus, chloro-benzene is readily nitrated, and yields three isomeric chloronitro-benzenes.

A derivative of this character is trinitrochloro-benzene, $C_6H_2 \cdot (NO_2)_3.Cl$, which acts like an acid chloride, and corresponds to $C_6H_2(NO_2)_3OH$, the so-called "picric acid" (see Trinitro-phenol, or Picric Acid).

V. AMIDO DERIVATIVES OF THE BENZENE HYDROCARBONS.

In studying these compounds it is necessary to remember that they can be looked at from two points of view: first, as benzene in which one or more atoms of hydrogen of the nucleus are replaced by the group NH_2, or as ammonia in which one or more hydrogen atoms are replaced by the radical C_6H_5, or similar aromatic hydrocarbon radical. Thus, $C_6H_5NH_2$ is called amido-benzene when looked at from the first point of view, or phenyl-amine when looked at from the second point of view, and considered as analogous to methylamine, $CH_3.NH_2$. Moreover, just as we had secondary and tertiary amines like dimethylamine and trimethylamine, so we have diphenylamine and triphenylamine. We have, also, the classes of monamines and diamines according as one or two molecules of ammonia are taken as the basis of replacement. The amido group NH_2 can also replace hydrogen of the side-group in the homologues of benzene.

In the accompanying tables we have indicated first the primary amines, which, containing the group NH_2, may also be called amido compounds, and then compared with these the secondary and tertiary amines, containing NH and N respectively, combined with aromatic radicals.

I. TABLE OF PRIMARY AMINES. AROMATIC AMIDO-DERIVATIVES.

From Benzene.	From Toluene.	From Xylene.	From Pseudo-cumene.
$C_6H_5.NH_2$, Aniline, b. p. 183°.	$C_6H_4(CH_3).NH_2$, Toluidines: *o-* b. p. 199°, *m-* 200°, *p-* 198°.	$C_6H_3(CH_3)_2.NH_2$, Xylidines; six isomers.	$C_6H_2(CH_3)_3.NH_2$, Pseudocumidine.
$C_6H_4(NO_2).NH_2$, Nitranilines.	$C_6H_5.(CH_2.NH_2)$, Benzylamine. $C_6H_5.(CH_2.CH_2.NH_2)$, Phenethylamine.		
$C_6H_4(NH_2)_2$, Phenylenediamine.	$C_6H_3(CH_3)(NH_2)_2$, Toluylenediamine.		
$C_6H_3(NH_2)_3$, Triamido-benzene.			

II. TABLE OF SECONDARY AND TERTIARY AMINES.

Secondary.	Tertiary.
$(C_6H_5)_2.NH$, Diphenylamine.	$(C_6H_5)_3N$, Triphenylamine.

Basic Substituted Amines.

$C_6H_5.NH.CH_3$, Methyl-aniline. $C_6H_5.NH.C_2H_5$, Ethyl-aniline. $(C_6H_5)_2N.NO$, Nitrosodiphenylamine.	$C_6H_5.N(CH_3)_2$, Dimethyl-aniline. $C_6H_5N(C_2H_5)_2$, Diethyl-aniline. $C_6H_4(NO).N(CH_3)_2$, Nitrosodimethyl-aniline.

Acid Substituted Amines (Anilids).

$C_6H_5.NH(C_2H_3O)$, Acetanilid. $(C_6H_5.NH)_2CO$, Carbanilid. $(C_6H_5NH)(NH_2)CS$, Phenyl-sulphurea.	$C_6H_5.N(CH_3)(C_2H_3O)$, Methyl-acetanilid. $(C_6H_5.N)CO$, Phenyl-cyanate. $(C_6H_5N)CS$, Phenyl mustard oil.

1. **Primary Monamines.**—This most i
formed most readily by the reduction of the
compounds in acid solution, as already menti
process used in the technical manufacture of a
logues. If a dinitro compound is taken, we
tial reduction a nitro-amido compound, such
mary monamines, with the NH_2 groups in t
benzylamine, are formed differently. These re
of ammonia upon such halogen derivatives as
in the side-group: $C_6H_5.CH_2Cl + NH_3 =$
HCl.

The determination as to whether the amid
tached to the nucleus or to the side-group
of two reactions: first, only those with the
side-chain result by the action of ammonia up
tive of a hydrocarbon; second, only the pr
the NH_2 group in the nucleus are changed
diazo compounds, according to the reaction

$$\underset{\text{Aniline Hydrochlorate.}}{C_6H_5NH_2.HCl} + HNO_2 = \underset{\text{Diazo-benzene C}}{C_6H_5{-}N{=}N}$$

Two other characteristic and important re
amines may be mentioned. By the action of
drides upon these amines the hydrogen of th
placed by an acid radical. These compounds

$$\underset{\text{Aniline.}}{C_6H_5NH_2} + \underset{\text{Acetic Acid.}}{CH_3COOH} = \underset{\text{Acetanilid}}{C_6H_5NH(C}$$

With chloroform and alcoholic potash solution
of the benzene series, just as those of the m
the fearful-smelling carbylamines (isonitriles):

$$C_6H_5NH_2 + CHCl_3 + 3KOH = C_6H_5{-}NC$$

Aniline (Amido-benzene or Phenylamine)
first obtained in 1826 from the dry distillatio
guese *anil*). It is also contained in coal-t
Colorless, oily liquid, turning yellow or brow
the air. Possesses a weak but peculiar odor.
solidifies at —8°. It has no action upon lit
base. It is poisonous, and is a good solvent fo
like indigo and sulphur. Unites like ammonia
to acids to form salts like $C_6H_5.NH_2.HCl$
H_2SO_4.

Small quantities of aniline in solution are recognized by the action of a solution of bleaching powder, which gives a violet color transient in character. A solution of aniline in concentrated sulphuric acid is first colored red and then deep blue by a grain of potassium bichromate. A solution of $K_2Cr_2O_7$, on the other hand, in acid solution of aniline sulphate produces a dark-green color, which in the end gives a precipitate of aniline black. The aqueous solution of aniline sulphate colors paper pulp made from wood-fibre intensely yellow. This is used as a test for wood-pulp in paper.

Substituted Anilines.—The modification of the aniline molecule may arise from the replacement of hydrogen of the nucleus by replacing groups, or by the replacement of the hydrogen in the amido group NH_2.

a. Substituted Anilines with Replacement in the Nucleus.—We may have according to theory three isomeric chloro-, bromo-, or iodo-anilines. These are of no present importance. We may have also three isomeric *Nitranilines*, $C_6H_4(NO_2)NH_2$. These all crystallize in yellow needles or prisms, readily soluble in alcohol, but only slightly soluble in water. They go into the phenylenediamines, $C_6H_4(NH_2)_2$, on reduction. They are also converted into nitrophenols when boiled with alkalies, ammonia being liberated.

Amido-benzene-sulphonic Acids, $C_6H_4(HSO_3).NH_2$.—By heating aniline with fuming sulphuric acid, as well as by the heating of aniline sulphate to 185° to 200°, the para acid, known as *Sulphanilic Acid*, is formed. It crystallizes with one molecule of water in somewhat difficultly soluble rhombic tablets. The meta acid, known as *Metanilic Acid*, finds application, as well as the sulphanilic acid, in the manufacture of azo dye-colors.

b. Substituted Anilines with Basic Groups in Side-Chain.—By the action of aniline chlorhydrate and an alcohol we have formed such compounds as:

Methyl-aniline, $C_6H_5.NH(CH_3)$, which is lighter than water, and has an odor like that of aniline, but stronger and more aromatic.

Dimethyl-aniline, $C_6H_5.N(CH_3)_2$, is an oil of sharp odor, solidifying at 0.5° and boiling at 192.6°. When oxidized with mild oxidizing agents it is changed into methyl violet, one of the aniline dyes. With benzo-trichloride, $C_6H_5.CCl_3$, dimethyl aniline reacts to form malachite green.

c. Substituted Anilines with Acid Groups in Side-Chain.—These are also known as *Anilids.* They are formed by the action of acid anhydrides or acid chlorides upon aniline.

Formanilid, $C_6H_5.NH(HCO)$, is obtained by the rapid distillation of 93 parts of aniline with 126 parts of crystallized or 90 parts of dehydrated oxalic acid: $C_2O_4H_2 + C_6H_5.NH_2 = H_2O + CO_2 + C_6H_5NH(HCO)$.

It forms colorless crystals, melting at 46°, tolerably easily soluble in water, easily soluble in alcohol. Is decomposed by dilute acids. Used for both external and internal use, as a local anæsthetic or as an antipyretic.

Acetanilid, $C_6H_5.NH(C_2H_3O)$ (**Acetanilidum, U.S.P.**).—100 parts of pure aniline and 100 parts of glacial acetic acid are boiled in a round-bottomed flask provided with inverted condenser for from one to two days, until a drop taken out for testing perfectly solidifies on cooling, or until a drop added to dilute caustic soda solution shows no free aniline. It is then fractionally distilled. When the water produced in the reaction has distilled off, the temperature, as shown by the thermometer, rises rapidly, and the Liebig condenser is changed for a straight glass tube, not cooled in any way, as otherwise the acetanilid solidifying in the tube would cause stoppage. The pure substance distils at 295°, and solidifies on cooling. It may be recrystallized out of boiling water. It forms colorless, odorless scales, neutral to test-paper, melting at 112°, and boiling, as said, at 295°. Difficultly soluble in cold water, more readily in hot water, readily in alcohol and ether. Is decomposed by hydrochloric acid into aniline and acetic acid. Heated with dry zinc chloride to 250°–270° it yields "flavaniline," $C_{16}H_{14}N_2$, a dye-stuff, dissolving in hydrochloric acid with moss-green color. First introduced under the name of "antifebrin," and largely used as an antipyretic and antineuralgic. In some cases it has been used for external use as an antiseptic.

Para-bromacetanilid, $C_6H_4BrNH(C_2H_3O)$, has been used in medicine under the name of "antisepsin" or "asepsin."

Methyl-acetanilid (Exalgin), $C_6H_5.N(CH_3)(C_2H_3O)$, is best made by the acetylating of monomethyl-aniline by a method analogous to that described for acetanilid, or by the action of methyl iodide upon sodium-acetanilid. Forms large crystalline needles, difficultly soluble in cold water, easily soluble both in dilute and concentrated alcohol. It fuses at 100°, boils between 240° and 250° without decomposition, and then solidifies in large hair-like crystals. Has been used as an antineuralgic.

Benzanilid, $C_6H_5.NH(C_6H_5CO)$, is formed by the action of benzoic anhydride or benzoyl chloride upon aniline. Colorless, pearly, lustrous scales, distilling without decomposition. Insoluble in water, moderately soluble in cold alcohol, more readily in hot alcohol. Used as an antipyretic.

Gallanilid, $C_6H_5.NH(C_6H_2(OH)_3CO)$. — Made by heating gallic acid with an excess of aniline for an hour to 150°. The pure compound fuses about 205°, and is difficultly soluble in cold water, more readily soluble in hot water, soluble in alcohol and ether. Has been used instead of pyrogallol in skin diseases for external application.

Toluidines, $C_6H_4(CH_3)NH_2$.—The three toluidines are formed by the reduction of the three nitro-toluenes. Para-toluidine, which is solid, and ortho-toluidine, which is liquid, are both present in coal-tar. In manufacturing commercial aniline by the reduction of commercial nitro-benzene, there is always formed a mixture of the two toluidines with aniline, as the original benzene is contaminated with toluene.

Xylidines, $C_6H_3(CH_3)_2NH_2$.—The six possible isomeric xylidines are all known. The technical xylidine contains several isomers, and is largely used for the manufacture of azo dye-stuffs.

Benzylamine, $C_6H_5CH_2.NH_2$, is isomeric with the toluidines. A colorless, basic liquid, boiling undecomposed. Formed most readily by heating benzyl chloride, $C_6H_5.CH_2Cl$, with acetamide, $NH_2(C_2H_3O)$, when the acetyl derivative is formed, from which the base may be obtained.

2. Secondary Monamines.—We have, as the first representative of this class:

Diphenylamine, $(C_6H_5)_2.NH$, which is obtained technically by heating aniline chlorhydrate with aniline under pressure :

$$C_6H_5NH_2.HCl + C_6H_5.NH_2 = C_6H_5.NH{-}C_6H_5 + NH_4Cl.$$

It forms white scales, with an agreeable odor of flowers, and a burning aromatic taste ; hardly soluble in water, easily soluble in alcohol, ether, and petroleum naphtha. A solution of diphenylamine in concentrated sulphuric acid is colored intensely blue by traces of nitric or nitrous acids, and hence is used for this purpose in water analysis.

The hexanitro derivative of diphenylamine, $C_{12}H_5(NO_2)_6N$, acts as a weak acid. Its ammonia salt is a yellow dye-stuff, known as "aurantia." Methyl-aniline and acetanilid and related compounds already considered may also be ranked as secondary monamines.

3. **Tertiary Monamines.**—The only compound to mention here is:

Triphenylamine, $N(C_6H_5)_3$.—It forms large leaflets, melting at 127°.

4. **Diamines and Triamines.**—The diamines may be formed by several reactions, the simplest of which is the reduction of the dinitro compounds. The three isomeric compounds may be distinguished from each other by characteristic reactions; thus, the meta diamines with nitrous acid give rise to a class of yellowish-brown azo dye-stuffs:

$$\underset{\text{Metaphenylene-diamine.}}{2C_6H_4(NH_2)_2} + HNO_2 = \underset{\text{Bismarck Brown.}}{C_{12}H_{13}N_5} + 2H_2O;$$

and the paradiamines when reduced with H_2S and then oxidized yield violet or blue sulphur-containing dye-stuffs of the methylene-blue class.

Metaphenylene-diamine, $C_6H_4\left\{\begin{matrix}NH_2\,(1)\\ NH_2\,(3)\end{matrix}\right.$, forms crystals melting at 63° and boiling at 276°–277°; difficultly soluble in water, easily in alcohol and ether. As traces of nitrous acid produce the reaction given above with the formation of a yellow dye, it constitutes a very delicate test for nitrous acid.

Paraphenylene-diamine, $C_6H_4\left\{\begin{matrix}NH_2\,(1)\\ NH_2\,(4)\end{matrix}\right.$, forms tablets fusing at 140° and boiling at 267°. When oxidized with ferric chloride or manganese oxide and sulphuric acid, quinone, $C_6H_4O_2$, is formed.

Toluylene-diamines, $C_6H_3(CH_3)(NH_2)_2$, and *Xylylene-diamines*, $C_6H_2(CH_3)_2(NH_2)_2$, are also known and used in the manufacture of dye-colors.

Triamido-benzene, $C_6H_3(NH_2)_3$, and *Tetramido-benzene*, $C_6H_2(NH_2)_4$, are representatives of triamines and tetramines respectively.

More special mention of the important dye-colors which are derived from the amines will be found under triphenyl-methane in a later section.

VI. DIAZO AND AZO COMPOUNDS. HYDRAZINES.

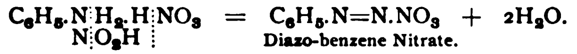
Both the diazo and the azo compounds contain the dyad group —N=N—. In the diazo compounds this group links together a hydrocarbon radical and an acid, in the azo compounds it links together two hydrocarbon radicals, as $C_6H_5—N=N—Cl$, diazo-benzene chloride, and $C_6H_5—N=N—C_6H_5$, azo-benzene.

1. **Diazo Compounds.**—This class is of very great scientific and technical interest, and its study has led to the discovery of the very numerous group of azo dye-colors, compounds formed by the reaction of the diazo bodies with the phenols and the amines.

To understand these diazo bodies let us compare the action of nitrous acid upon the primary amines of the methane series and the benzene series respectively. The former are converted into alcohols without the formation of intermediate products, according to the reaction:

$$C_2H_5.NH_2 + NOOH = C_2H_5.OH + N_2 + H_2O.$$

The latter can undergo an analogous change, but there result in their case well-characterized intermediate products, these so-called diazo compounds. Thus:



$$\begin{array}{l} C_6H_5.N\vdots H_2.H\vdots NO_3 \\ \quad\; N\vdots O_2H\ \vdots \end{array} = \underset{\text{Diazo-benzene Nitrate.}}{C_6H_5.N{=}N.NO_3} + 2H_2O.$$

This reaction is carried out in the cold, in fact in a carefully-cooled solution. If the solution is warmed, the reaction goes on to the end result indicated with the other class of amines and a phenol is formed:

$$C_6H_5.N=N.NO_3 + H.OH = C_6H_5.OH + N_2 + HNO_3.$$

Just as the salts of the primary monamines when treated with nitrous acid yield the diazo compounds, so when primary diamines are treated with nitrous acid we obtain *tetrazo compounds*, also of great value as dye-stuffs, particularly for cotton dyeing.

Besides the reaction whereby on heating in solution the diazo compounds decompose with the formation of a phenol, we have a second equally important one. When their salts are heated with alcohol they are changed into the corresponding hydrocarbons with liberation of nitrogen:

$$C_6H_5.N=N.Cl + C_2H_5OH = C_6H_6 + N_2 + HCl + C_2H_4O.$$

By means of these two reactions it is possible to change from an amido compound into either a phenol or back to the original hydrocarbon. Hence their great importance in the synthetic work of organic chemistry. The salts of the diazo compounds are mostly colorless crystalline bodies, which are explosive in dry condition and decompose on strong heating of their aqueous solutions.

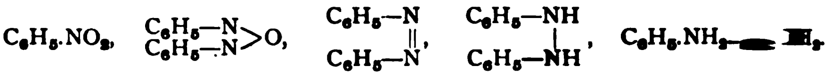
Diazo-benzene Chloride, $C_6H_5.N{=}N.Cl$. — Stable only in solution.

Diazo-benzene Nitrate, $C_6H_5N{=}N.NO_3$.—Colorless needles, very explosive.

Diazo-benzene Sulphate, $C_6H_5N{=}N.HSO_4$.—Prisms which explode at 160°.

The free *diazo-benzene*, $C_6H_5N{=}N{-}(OH)$, is a heavy oil of yellow color and aromatic odor, which decomposes easily with liberation of nitrogen.

2. **Azo Compounds.**—While the reduction of nitro compounds in acid solution leads to the aromatic amines, the use of alkaline reducing agents, such as sodium amalgam, zinc-dust and caustic soda, and potash and alcohol, gives rise to intermediate products. The connection of these with the starting-point nitro-benzene and the end product aniline is shown in the following formulas:



$$C_6H_5.NO_2,\quad \begin{matrix}C_6H_5{-}N\\C_6H_5{-}N\end{matrix}{>}O,\quad \begin{matrix}C_6H_5{-}N\\ \|\\ C_6H_5{-}N\end{matrix},\quad \begin{matrix}C_6H_5{-}NH\\ |\\ C_6H_5{-}NH\end{matrix},\quad C_6H_5.NH_2.$$

Azoxy-benzene. Azo-benzene. Hydrazo-benzene.

These three intermediate classes are usually grouped together under the general name of azo compounds.

From azo-benzene, $C_6H_5{-}N{=}N{-}C_6H_5$, may be obtained two important classes of colored derivatives, which are of great value under the name of *azo dye-colors*. By the introduction of the amido group in the place of a hydrogen atom we obtain the amido-azo compounds like $C_6H_5.N{=}N.C_6H_4NH_2$, amido-azo-benzene; by the introduction of the hydroxyl group in the place of a hydrogen atom we obtain the oxyazo compounds like $C_6H_5.N{=}N{-}C_6H_4(OH)$, oxyazo-benzene. These are formed respectively, as mentioned on p. 701, by the action of an amine upon the diazo compounds and the action of a phenol upon the same.

Most of these azo dyes are insoluble in water, but all can be converted by the action of strong sulphuric acid into the corresponding sulphonic acids, and both these and their alkaline salts are soluble in water.

The dyes which are derivatives of amidoazo-benzene are termed "Chrysoïdines," and those which are derivatives of oxyazo-benzene are termed "Tropæölines."

3. **Hydrazines.**—The aromatic hydrazines, like those in the methane series, are derivatives of hydrazine, $NH_2{-}NH_2$, formed by the replacement of the hydrogen atoms by alcohol radicals.

case where the OH group replaces a hydrogen atom of the nucleus and where it replaces a hydrogen atom of the side-group. In the former case the compounds are called *phenols*, and in the latter *aromatic alcohols*. As the latter contain the group —$CH_2.OH$ characteristic of primary alcohols (see p. 571), they can be oxidized to aldehydes and acids, while the former, which are more like tertiary alcohols, cannot be oxidized without entire decomposition of the molecule.

According to the number of the OH groups introduced in place of hydrogen of the nucleus, we have monatomic, diatomic, triatomic, etc., phenols.

TABULAR VIEW OF THE MORE IMPORTANT PHENOLS.

Monatomic.	Diatomic.	Triatomic.
$C_6H_5.OH$, Phenol, m. p. 42°, b. p. 181°.	$C_6H_4(OH)_2$, Dioxy-benzenes: *o-* = Pyrocatechin, 104°–245°; *m-* = Resorcin, 118°–280°; *p-* = Hydroquinone, 169°.	$C_6H_3(OH)_3$, Trioxy-benzenes: *v-* = Pyrogallol, 115°–210°; *a-* = Oxyhydroquinone, 140.5°; *s-* = Phloroglucin, 217°.
$C_6H_4(CH_3).OH$, Cresols, *o-* 31°–188°, *m-* 3°–201°, *p-* 36°–198°.	$C_6H_3(CH_3).(OH)_2$, Dioxytoluenes: 1:3:5 = Orcin, 107°–288°; 1:3:4 = Homopyrocatechin.	$C_6H_2(CH_3)(OH)_3$, Methyl-pyrogallol.
$C_6H_3(CH_3)_2OH$, Xylenols.	$C_6H_2(CH_3)_2(OH)_2$, Xylorcin.	
$C_6H_2(CH_3)_3OH$, Pseudo-cumenols.	$C_6H(CH_3)_3.(OH)_2$, Mesorcin.	
$C_6H(CH_3)_4.OH$, Durenols.		
Isomeric with these are: $C_6H_3(CH_3)(C_3H_7).OH$, Thymol, Carvacrol.	**Tetratomic Phenols.**	**Hexatomic Phenols.**
$C_6(CH_3)_5OH$, Pentamethyl-phenol.	$C_6H_2(OH)_4$, Tetraoxy-benzene.	$C_6(OH)_6$, Hexaoxy-benzene.

The phenols in chemical character stand between the true alcohols and the organic acids. They combine to form mixed ethers, like anisol, $C_6H_5.OCH_3$, or esters, like phenyl-sulphuric acid, $C_6H_5—OSO_3H$. At the same time they have the character of weak acids, and form salts with the metals, like $C_6H_5.ONa$, sodium-phenol. The acid character is notably increased by the entrance of NO_2 groups, as in trinitro-phenol (picric acid), $C_6H_2(NO_2)_3.OH$.

Phenols are formed by the dry distillation of many organic substances. Thus, phenol and cresol and their homologues are found in coal-tar and in various wood-tars. They are also formed artificially by numerous reactions, among which may be mentioned:

1. By the fusion of the sulpho acids of the aromatic hydrocarbons with caustic potash, $C_6H_5HSO_3 + 2KOH = C_6H_5.OH + K_2SO_3 + H_2O$.

2. By the action of nitrous acid upon the amido compounds and boiling the diazo compounds which first form with water. The two reactions are:

$$(a)\ C_6H_5NH_2HCl + HNO_2 = C_6H_5N{=}N{-}Cl + 2H_2O.$$
$$(b)\ C_6H_5.N{=}N.Cl + H_2O = C_6H_5.OH + N_2 + HCl.$$

3. By the dry distillation of the aromatic phenol-acids (oxy-acids) either with or without lime:

$$\underset{\text{Gallic Acid.}}{C_6H_2(OH)_3.COOH} = \underset{\text{Pyrogallol.}}{C_6H_3(OH)_3} + CO_2.$$

Among the most characteristic reactions of the phenols may be mentioned:

1. The formation of the several classes of derivatives already referred to, in which the H of the hydroxyl is replaced,—viz., phenolates, phenol-ethers, and phenol-esters.

2. The formation of substitution compounds in which hydrogen of the nucleus is replaced by chlorine, bromine, nitro, or sulphonic group.

3. The sodium and potassium phenolates unite with CO_2, when heated under pressure, to form salts of oxyacids:

$$\underset{\text{Sodium Phenol.}}{C_6H_5ONa} + CO_2 = \underset{\text{Sodium Salicylate.}}{C_6H_4(OH)COONa}.$$

4. Many phenols give characteristic colors when ferric chloride is added to their neutral solutions. Thus, with ferric chloride phenol and resorcin give a violet color, pyrocatechin a green color, orcin a blue-violet, and pyrogallol a red color.

1. **Monatomic Phenols.**—From benzene but one monatomic phenol is derived.

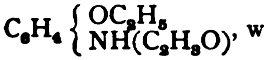
Phenol, $C_6H_5.OH$ (**Acidum Carbolicum**, U. S. P.), was discovered in 1834 in coal-tar. It is found in the urine of herbivora and of man (as phenyl-sulphuric acid), in castoreum, in bone oil and in coal- and wood-tar. It forms colorless, crystalline needles fusing at 42°, and boiling at 181°. A small percentage of wat liquefies the crystals and keeps it in liquid condition. It is soluble in 15 parts of water at ordinary temperatures, easily soluble in hot water, in alcohol, ether, glycerin, fixed oils, potash, a ammonia; has a strong and characteristic odor, burning tas and caustic action on the skin. It is a strong antiseptic, even the impure state (**Acidum Carbolicum Crudum, U. S. P.**) when it contains considerable cresols and higher phenols. Ferric chloride colors it even in dilute solution violet. Bromine water causes a white precipitate of tribrom-phenol. It unites with the alkalies and other bases to form the so-called "carbolates," as $C_6H_5.ONa$.

A number of important derivatives of phenol are known.

Both chlorine and bromine readily form substitution compounds with phenol, such as *Trichlor-phenol*, $C_6H_2Cl_3.OH$, and *Tribrom-phenol*, $C_6H_2Br_3.OH$. Both of these are distinguished by their antiseptic and healing power, and have been recommended in medicine. The former is a gas of sharp, penetrating odor, and the latter is a white, crystalline solid, melting at 95°.

Nitro Phenols.—Mono- and dinitro-phenols are known, but the only important compound to note is *trinitro-phenol* (or picric acid). This is formed by the action of fuming nitric acid upon many organic substances, such as indigo, silk, leather, wool, etc. It is ordinarily prepared by the nitration of phenol in the presence of strong sulphuric acid. It crystallizes out of water or alcohol in pale-yellow scales, and out of ether in prismatic needles, which have a bitter taste. It melts at 122.5°, and can be sublimed without decomposition, but on rapid heating it is instantly decomposed with slight explosion. It is an important yellow dye. Its salts are beautifully crystallized, but very explosive when heated or struck. The potassium and ammonium salts are used in various explosive mixtures. Picric acid also forms well-crystallized addition compounds with many of the higher hydrocarbons, as naphthalene and anthracene.

Amido Phenols are formed by the reduction of the corresponding nitro phenols. From para-amido-phenol, $C_6H_4(OH)NH_2$, several important derivatives are obtained. The ethyl ethers of the amido-phenols are called "phenetidins." From the para-amido-phenol just mentioned we obtain then para-phenetidin,

$C_6H_4\left\{\begin{matrix}OC_2H_5\\NH_2\end{matrix}\right.$. When this is treated with glacial acetic acid the acetyl group is introduced, and we obtain *acetpara-phenetidin*,  $C_6H_4\left\{\begin{matrix}OC_2H_5\\NH(C_2H_3O)\end{matrix}\right.$, which has been brought into medical use under the name of "phenacetin." It forms white, lustrous crystals, without odor and almost without taste, melting at 135°. It is difficultly soluble in cold water, more readily soluble in alcohol. Phenacetin is one of the best known of the newer antipyretics and antineuralgics.

Related to phenacetin are "phenocoll," which is glycocoll-phenetidin, $C_6H_4\left\{\begin{matrix}OC_2H_5\\NH.COCH_2NH_2\end{matrix}\right.$, the commercial preparation being the chlorhydrate, and "methacetin" or para-acetanisidin, $C_6H_4\left\{\begin{matrix}OCH_3\\NH.C_2H_3O\end{matrix}\right.$.

Phenol-sulphonic Acids are formed by the action of concentrated sulphuric acid upon phenol at low temperatures. The ortho-phenol-sulphonic acid is used in 33⅓-per-cent. solution as an antiseptic, under the name of "aseptol" or "sozolic acid." On keeping, it gradually changes into the isomeric para-phenol-sulphonic acid, which change is also readily effected by heating its solutions. The para acid yields well-crystallized salts, two of which are well known in medicine. The sodium salt, $C_6H_4\left\{\begin{matrix}OH\\SO_3Na\end{matrix}\right.+2H_2O$ (**Sodii Sulphocarbolas,** U.S.P.), forms colorless, rhombic prisms, odorless, and with a cooling, saline and slightly bitter taste. The zinc salt, $Zn(C_6H_5SO_4)_2 + 2H_2O$, which is official in the British Pharmacopœia, forms colorless, tabular efflorescent crystals. By the action of a mixture of potassium iodide and iodate upon the para-phenol-sulphonic acid is obtained the potassium salt of diiodo-para-phenol-sulphonic acid, which, along with other salts of the same acid, has been introduced into medicine under the name of "soziodol" compounds. They are used as antiseptics and substitutes for iodoform for external use.

Anisol (phenyl-methyl ether), $C_6H_5.OCH_3$, and *Phenetol* (phenyl-ethyl ether), $C_6H_5.OC_2H_5$, are obtained by heating phenol and caustic potash with either methyl or ethyl iodide in alcoholic solution. They are liquids of ethereal odor, the former boiling at 152°, and the latter at 172°.

Cresols, $C_6H_4(CH_3)OH$, are the first homologues of phenol. All three of these compounds are present in coal-tar, and are also contained in the tar from pine and beech wood. Crude carbolic acid always contains a mixture of these, known technically as "cresylic acids." Ortho-cresol is found in the form of its sulphuric ester in the urine of horses; para-cresol is produced by the decay of albumen (tyrosin), and is found in human urine. Its dinitro compound is a golden-yellow dye, which is used as ammonium or potassium salt under the name of "Victoria orange." Meta-cresol is said to be the most powerful antiseptic, exceeding phenol in power, but is much more poisonous. A derivative of this latter is the triiodo-meta-cresol, $C_6HI_3(CH_3)OH$, introduced into medicine under the name of "losophan."

Thymol, U. S. P., is para-propyl-meta-cresol, $C_6H_3.\overset{1}{CH_3}.\overset{3}{OH}.\overset{4}{C_3H_7}$. It is a phenol found naturally occurring in a number of essential oils. It forms large, colorless, translucent crystals, with an aromatic, thyme-like odor and pungent, aromatic taste. It melts at 50°–51°, and boils at 228°–230°. When triturated with equal quantities of camphor, menthol, or chloral hydrate, it liquefies. It is difficultly soluble in water, readily soluble in alcohol, ether, or chloroform. A derivative of thymol is dithymoldiiodide, $C_{20}H_{24}O_2I_2$, which has been introduced into medicine under the name of "aristol." It is a light, chocolate-colored powder, almost without odor or taste, and is used as a substitute for iodoform.

Isomeric with thymol is *carvacrol*, which is para-propyl-ortho-cresol, $C_6H_3.\overset{1}{CH_3}.\overset{2}{OH}.\overset{4}{C_3H_7}$. It is present in oil of *Origanum hirtum*, and may be prepared by heating camphor with iodine.

Xylenols, $C_6H_3(CH_3)_2OH$. — Of the six possible isomers, *m*-xylenol is found in the creosote of beech-wood tar.

2. **Diatomic Phenols.**—These compounds containing two hydroxyl groups are formed by methods analogous to those given for the monatomic phenols, especially by the method of fusion of the sulphonic acids with potash.

Pyrocatechin, $C_6H_4(OH)_2$, is the ortho compound. It was first formed by the dry distillation of catechin (mimosa catechu), whence the name. It is present in small amounts in human urine, and is formed by the dry distillation of wood, by heating cane sugar, cellulose, and starch with water to 200°–280°. It is also formed by the fusion of many resins with potash. It crystallizes in short, rhombic prisms, which can be sublimed, and are readily soluble in water, alcohol, and ether. The aqueous solution is colored green with ferric chloride and then violet by ammonia.

Orcin, $C_6H_3(CH_3)(OH)_2$, is a dioxy-toluene. It is found in many lichens (*Rocella tinctoria*, *Lecanora*, etc.). It is formed when aloes are fused with caustic potash, and can be made synthetically from toluene, by fusing *m*-dibrom-toluene with potash at 280°. It crystallizes in colorless prisms, which turn red. The ammoniacal solution absorbs oxygen from the air, and yields *orceïn*, $C_7H_7NO_3$, the chief constituent of commercial archil dye. Related to this latter coloring matter is also *litmus*, the well-known blue vegetable color.

Homo-pyrocatechin, $C_6H_3(CH_3)(OH)_2$, is an isomeric dioxy-toluene. Its methyl-ether is *creosol*, $C_6H_3(CH_3),\begin{cases}OH,\\OCH_3,\end{cases}$ one of the chief constituents, along with guaiacol, of the creosote of beech-wood-tar.

Eugenol, the chief constituent of oil of cloves, is the methyl-ether of an unsaturated phenol, $C_6H_3(OH)_2(CH_2.CH{=}CH_2)$.

3. **Triatomic Phenols.**—Of the three isomeric trioxy-benzenes, the most important is *Pyrogallol*, $C_6H_3(OH)_3$ (**Pyrogallol, U. S. P.**). It is obtained generally by the dry distillation of gallic acid: $C_6H_2(OH)_3COOH = C_6H_3(OH)_3 + CO_2$. It forms light, white, shining laminæ, odorless, and with a bitter taste. It becomes darker on exposure to air and light. It is soluble in water, alcohol, and ether. Its solutions, especially when alkaline, absorb oxygen from the air and turn brown in color. Because of this reaction it is used in gas analysis to absorb free oxygen from gaseous mixtures. This reducing power is also recognized with silver, gold, and mercury solutions. It is largely used in photography as a developer because of this power of reduction of silver salts. Pyrogallol also combines with phthalic anhydride to form the dye-color "galleïn."

Phloroglucin, $C_6H_3(OH)_3$, an isomeric trioxy-benzene, is produced in the decomposition of phloretin, a glucoside, and by the fusion of a number of resins (such as gamboge, dragon's blood, catechu, and kino) with caustic potash. It is also obtained synthetically by the fusion of benzene-trisulphonic acid with potash. It forms large prisms, which sublime without decomposition, melting at 218°. With ferric chloride it gives a dark-violet coloration. Phloroglucin colors a pine shaving, moistened with hydrochloric acid, red, and is used for the detection of lignin or wood-fibre in paper, etc.

Oxyhydro-quinone, $C_6H_3(OH)_3$, the third isomeric trioxy-benzene, results from the fusion of hydro-quinone with potash.

4. Tetratomic Phenols.—A tetroxy-benzene, $C_6H_2(OH)_4$, has been prepared from succino-succinic ether. It crystallizes in yellow needles, and is stable when pure.

5. Pentatomic Phenols.—As hexahydro derivatives of a pentatomic phenol, $C_6H(OH)_5$, we must include several compounds which at one time were considered to be pentatomic alcohols, or to belong to the carbohydrates.

Quercite, $C_6H(OH)_5.H_6$.—A sweet-tasting crystalline principle extracted from the oak. It forms colorless monoclinic crystals, melting at 235°.

Pinite, $C_6H(OH)_5.H_6$, is found in the exudation of the California pine (*Pinus lambertiana*). It forms colorless crystals, easily soluble in water, and fusing at over 150°.

Inosite (Phaseomannite), $C_6H_{12}O_6 + 2H_2O$, is found in small amount in the muscular tissue, in the heart, lungs, liver, spleen, kidneys, and brain ; the urine also contains inosite after abundant water drinking.

It is also contained in plants, as green beans, peas, lentils, and grape juice. It crystallizes in rhombic plates, which crumble in the air. Soluble in water, insoluble in alcohol. Melts at 210°. It has no reducing power, nor is it fermentable.

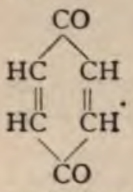
6. Hexatomic Phenols.—We have a derivative of the normal hexaoxy-benzene, $C_6(OH)_6$, in the so-called potassium carbon monoxide, formed in the distillation of metallic potassium, which has the formula $C_6(OK)$. The phenol itself has also been prepared synthetically. It forms small, grayish-white needles, which acquire a reddish color on exposure to the air. They are not fusible, but decompose at about 200°.

Phenose is a hexatomic phenol of hexahydro-benzene, and has the formula $C_6H_6(OH)_6$. It has been obtained by the action of soda solution upon the hypochlorous acid addition product of benzene, $C_6H_6\left\{\begin{matrix}Cl_3\\(OH)_3\end{matrix}\right.$. It is an amorphous, readily soluble, and deliquescent substance. It is much like the glucoses, has a sweet taste, and reduces Fehling's solution, but is not capable of fermentation.

7. Quinones.—This term is applied to a class of benzene derivatives in which two hydrogen atoms seem to be replaced by two oxygen atoms. Not only benzene, but especially the condensed aromatic hydrocarbons, naphthalene, anthracene, phenanthrene, chrysene, etc., when oxidized by chromic acid in glacial acetic acid solution, yield quinones. They are formed also by the oxi-

dation of a number of derivatives of benzene in whic
placing groups occupy the para position. Thus, hydr
(paradioxy-benzene), sulphanilic acid (*p*-amido-be
phonic acid), and phenylene-diamine, as well as pheno
line, all yield quinone when oxidized by chromic acid.

The constitution of quinone, $C_6H_4O_2$, is not definite
By some it is written $C_6H_4\left\{\begin{matrix}O\\O\end{matrix}\right>$ and by others C_6I



. According to the first of these formulas
would be a peroxide, according to the second a keto
benzene itself, but of a dihydro-benzene. This latter vi
generally accepted, as it brings it into analogy with a
none and the other higher quinones which are kno
diketones.

Quinone (Benzo-quinone), $C_6H_4O_2$, is made most r
oxidizing aniline sulphate with chromate of potash and
acid. The quinone so formed is shaken out with ether.
prisms melting at 115.7° and subliming. It has a chl
odor, is difficultly soluble in cold water, more readily
hot water, as well as in alcohol and ether. It is easily
into hydroquinone by reducing agents like SO_2 or HI.

By chlorinating quinone, or by the action of potassi
rate and hydrochloric acid upon phenol, we obtain *tetra*
none (chloranil), $C_6Cl_4O_2$. As reducing agents convert
into tetrachlorhydro-quinone, it is used as an oxidizing
the manufacture of aniline colors, as with methyl-violet.
of the homologues of quinone may also be mentioned,
quinone, $C_6H_3(O_2)(CH_3)$, Xylo-quinone, $C_6H_2(O_2)$(C
Thymo-quinone, $C_6H_2(O_2)\left\{\begin{matrix}CH_3\\C_3H_7\end{matrix}\right.$.

VIII. AROMATIC ALCOHOLS, ALDEHYDES, AND K

1. Aromatic Alcohols.—The aromatic alcohols diff
fore stated, from the phenols in that the OH has replace
gen in the side-group instead of hydrogen in the nucleu
may be, and often are, isomeric with phenols, as benzyl
$C_6H_5.CH_2OH$, and cresol, $C_6H_4(CH_3).OH$.

responding ketone, $C_6H_5.CO.CH_3$ (acetophenone), and on careful oxidation reproduces this compound.

Phenyl-propyl Alcohol (Hydrocinnamyl Alcohol), $C_6H_5.CH_2.CH_2.CH_2OH$, is obtained from cinnamyl alcohol by reduction. It exists as cinnamic ester in storax. Closely related to this is the unsaturated aromatic alcohol, known as

Cinnamyl Alcohol (Styrene), $C_6H_5.CH{=}CH.CH_2OH$.—This occurs as cinnamic ester under the name of styracine in storax resin (**Styrax,** U. S. P.). It crystallizes in shining needles, is sparingly soluble in water, and possesses a hyacinth-like odor It melts at 33° and distils at 250°. On careful oxidation it yields cinnamic acid; more energetically oxidized it yields benzoic acid.

2. Aromatic Aldehydes.—These correspond in all their general properties with the aldehydes of the methane series.

Benzaldehyde, $C_6H_5.COH$ (**Oleum Amygdalæ Amaræ,** U.S. P.)—This compound was at one time exclusively obtained by the decomposition of the glucoside amygdalin of the bitter almond in the presence of emulsin and other ferments, according to the reaction $C_{20}H_{27}NO_{11} + 2H_2O = C_6H_5.COH + 2C_6H_{12}O_6 + HCN$. It is now mostly made artificially by the oxidation of the chlorine derivatives of toluene:

$$\underset{\text{Benzyl Chloride.}}{2C_6H_5CH_2Cl} + \underset{\text{Benzal Chloride.}}{C_6H_5CHCl_2} + 2MnO_2 = \underset{\text{Benzaldehyde.}}{3C_6H_5.COH} + 2MnCl_2 + H_2O,$$

or by heating benzal chloride with milk of lime under pressure. This reaction has been already noted under benzal chloride (see p. 691).

Benzaldehyde is a colorless, strongly-refracting liquid of pleasant bitter-almond odor. Boils at 179°, and has a sp. gr. of 1.05. It is only slightly soluble in water, but is easily soluble in alcohol and ether. Its behavior shows in many ways its character as an aldehyde. It is easily oxidized to the corresponding acid; it reduces silver solutions with the formation of a metallic mirror; it may be reduced to a primary alcohol; it forms a crystalline compound with sodium bisulphite; it reacts with hydroxylamine and phenyl-hydrazine. A reaction which is distinct and quite characteristic of it as an aromatic aldehyde is its power to unite to form condensation products. Thus, we are able to effect the synthesis of cinnamic acid by the condensation of benzaldehyde and sodium acetate, $C_6H_5.COH + CH_3COONa = C_6H_5CH{=}CH.COONa + H_2O$, a reaction of the greatest importance in the manufacture of artificial indigo (see Indigo).

later under diphenyl-methane. The diatomic and triatomic phenols also react with glacial acetic acid in the presence of zinc chloride to a class of ketones known as keto-phenols.

Gallaceto-phenone, $C_6H_2(OH)_3.COCH_3$, is formed by the reaction between pyrogallol and glacial acetic acid in the presence of zinc chloride. It forms a dirty-flesh-colored, crystalline powder, difficultly soluble in cold water, easily soluble in hot water, alcohol, or ether, and in glycerin. It melts at 170°. It is used in medicine as a substitute for pyrogallol, being relatively non-poisonous, and at the same time strongly antiseptic against micro-organisms.

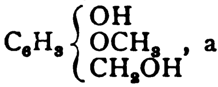
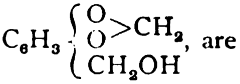
IX. PHENOL ALCOHOLS AND PHENOL ALDEHYDES.

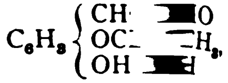
1. **Phenol Alcohols.**—These compounds, as the name indicates, partake of both phenol and aromatic alcohol character; that is, they must contain at least two OH groups, one of which (the phenolic OH) is directly attached to the nucleus, and the other (the alcoholic OH) is contained in the side-group, which will then be CH_2OH. The empirical formulas of the phenol alcohols will always differ by one additional oxygen atom from the aromatic alcohols to which they correspond. Hence they are often called "oxy alcohols."

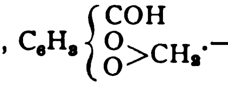
Oxy-benzyl Alcohols, $C_6H_4(OH)CH_2OH$.—Of the three isomeric compounds of this formula the ortho compound is best known. It is *Saligenin*, which results when the glucoside salicin is decomposed by emulsin or dilute acids: $C_{13}H_{18}O_7 + H_2O = C_6H_4(OH)CH_2OH + C_6H_{12}O_6$.

It forms pearly tablets soluble in hot water, alcohol, and ether, melting at 82°, and subliming near 100°. It yields salicylic acid when oxidized.

Anisyl Alcohol, $C_6H_4(OCH_3)CH_2OH$, is the methyl ether of the *p*-oxybenzyl alcohol, and is obtained from anisic aldehyde by alcoholic potassium hydrate. It crystallizes in needles, melting at 25° and boiling at 259° without decomposition. When oxidized it yields anisic aldehyde and acid.

Vanillin Alcohol,  $C_6H_3\begin{cases}OH\\OCH_3\\CH_2OH\end{cases}$, and *Piperonyl Alcohol*,  $C_6H_3\begin{cases}\begin{matrix}O\\O\end{matrix}>CH_2\\CH_2OH\end{cases}$, are formed from their aldehydes vanillin and piperonal by acting on their solutions with sodium amalgam.

Vanillin (Methyl-protocatechuic Aldehyde),  $C_6H_3\left\{\begin{matrix}CHO\\OCH_3,\\OH\end{matrix}\right.$ is the odoriferous principle of the vanilla bean, which contains from 2 to 2½ per cent., and is found also in many crude beet-sugars, in asparagus, asafœtida, and in small amount in the woody tissue of many plants. It was first made artificially by Tiemann and Haarmann by oxidizing coniferin, a glucoside contained in the cambial juice of the Coniferæ, with chromic acid. It is also formed synthetically together with an isomeric aldehyde (iso-vanillin) when guaiacol is acted upon with chloroform and alkali, and by oxidizing eugenol from oil of cloves. Vanillin crystallizes in needles, and is soluble in water, alcohol, ether, carbon disulphide, and chloroform. It melts at 80° and boils at 285°. Heated with HCl to 180° it decomposes into methyl chloride and protocatechuic aldehyde. Ferric chloride colors its solution blue.

Piperonal (Heliotropine),  $C_6H_3\left\{\begin{matrix}COH\\O\\O\end{matrix}\right.\!\!>CH_2$.—This is the methylene ether of protocatechuic aldehyde. It is obtained by oxidizing piperic acid. Forms small, colorless, shining crystals smelling of coumarin, and difficultly soluble in water, but readily soluble in alcohol, ether, vaseline, and glycerin. Melts at 37° and boils at 263°. Is largely used in perfumery as artificial heliotropine.

X. AROMATIC ACIDS AND PHENOL ACIDS.

The aromatic acids, like the fatty acids and other acids of the methane series, contain one or more carboxylic groups, COOH, in this case linked either directly or indirectly with the phenyl group or the benzene nucleus. This group COOH, of course, presupposes the side-group CH_3, from which it is formed by oxidation.

TABLE OF AROMATIC ACIDS AND PHENOL ACIDS.

Monobasic Saturated Acids:	Melting Point.
Benzoic acid, $C_6H_5.COOH$	121°
Phenylacetic acid, $C_6H_5.CH_2.COOH$	76°
Toluic acids, $C_6H_4(CH_3).COOH$	*o*- 102° *m*- 110° *p*- 180°
Hydrocinnamic acid, $C_6H_5.CH_2.CH_2.COOH$	49°
Mesitylenic acid, $C_6H_3(CH_3)_2COOH$	166°
Xylylic acids, $C_6H_3(CH_3)_2COOH$	126° 163°
Cumic acid, $C_6H_4(C_3H_7)COOH$	116°

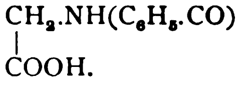
Benzoic Acid, $C_6H_5.COOH$ (**Acidum Benzoicum**, U. S. P.), was discovered in 1608 in gum benzoïn, and prepared from urine by Scheele in 1785. It occurs in the free state in a number of resins and balsams, as gum benzoïn, Peru balsam, Tolu balsam, dragon's blood, and in certain plants. In the urine, especially of carnivorous animals, it occurs as hippuric acid. It is prepared either by sublimation from the gum-resin (*acidum ex resina*), or by the decomposition of hippuric acid (*acidum ex urina*), or synthetically starting from toluene (*acidum ex toluole*). The reaction for this latter production, $C_6H_5CCl_3 + 2H_2O = C_6H_5.COOH + 3HCl$, has already been referred to (see p. 691).

Benzoic acid forms white, lustrous scales, melting at 121°, boiling at 250°, and subliming in a current of steam. The vapors have a peculiar odor, exciting to sneezing and coughing. It is difficultly soluble in cold water, readily soluble in hot water, alcohol, benzene, and petroleum ether.

Of the metallic benzoates we have, as official compounds, **Ammonii Benzoas**, U. S. P., $NH_4C_7H_5O_2$, **Lithii Benzoas**, U. S. P., $LiC_7H_5O_2$, and **Sodii Benzoas**, U. S. P., $NaC_7H_5O_2$. The mercury and bismuth benzoates have also been used in medicine. Both the methyl and the ethyl esters of benzoic acid, $C_6H_5.COOCH_3$ and $C_6H_5.COOC_2H_5$ respectively, are known as pleasant-smelling aromatic liquids, the latter especially, under the name of "benzoic ether," is used in some artificial fruit essences.

Other derivatives of benzoic acid are: benzoyl chloride, $C_6H_5.COCl$, benzonitrile (or phenyl cyanide), $C_6H_5.CN$, benzoic anhydride, $(C_6H_5CO)_2O$, benzamide, $C_6H_5.CONH_2$, and benzanilid, $C_6H_5.CO.NHC_6H_5$. This latter compound is the analogue of acetanilid, and has been introduced into medicine as an antipyretic possessing some advantages over acetanilid.

An important derivative of benzoic acid, and at the same time one of the commercial sources of it, is ***hippuric acid*** (benzoyl-glycocoll),



$$\begin{array}{l} CH_2.NH(C_6H_5.CO) \\ | \\ COOH. \end{array}$$

This compound is obtained from the urine of the herbivora, and in case benzoic acid or compounds capable of yielding it by oxidation are taken internally, from human urine as well. It may be formed artificially by the reaction of benzoyl chloride and glycocoll in the presence of caustic alkali:

$$C_6H_5.COCl + CH_2(NH_2)COOH = C_6H_5CO.NH.CH_2COOH + HCl$$

decay of albuminous matter. It forms fine needles, melting at 47° and boiling at 280°.

Cumic Acid (*p*-Isopropyl-benzoic Acid), $C_6H_4(C_3H_7)COOH$, is obtained by oxidizing Roman oil of cumin with potassium permanganate. It also results from the oxidation of cymene in the animal organism. It crystallizes in plates, and yields cumene when distilled with lime.

2. **Polybasic Saturated Acids.**—By the oxidation of two or more of the side-groups in the homologues of benzene, polybasic acids are obtained.

Phthalic Acids (Benzene-dicarboxylic Acids), $C_6H_4(COOH)_2$.—We have here three isomers: orthophthalic acid, isophthalic acid, and terephthalic acid. The first is in all respects the most important. It forms when orthoxylene is oxidized by nitric acid or potassium permanganate (not by chromic acid, however, which decomposes it) or any ortho-di-derivative of benzene. It is made on a large scale by the oxidation of naphthalene, either directly with nitric acid or by first forming the tetrachlor-naphthalene, $C_{10}H_8Cl_4$, and then oxidizing this with nitric acid. It crystallizes in short prisms or plates, melting at 184°; readily soluble in water, alcohol, and ether. When heated above its melting point, it readily loses water and yields the anhydride. Distilled with lime it loses CO_2 and yields benzene.

Phthalic Anhydride, $C_6H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\}>O$.—This compound is obtained by sublimation in long, white prisms, melting at 128° and boiling at 284°. When heated with the phenols it yields a series of compounds known as "phthaleïns," such as phenolphthaleïn, resorcinphthaleïn (fluoresceïn), etc. These will be referred to again under Triphenyl-methane and derivatives.

Terephthalic Acid is the para compound. It results from the oxidation of *p*-xylene, cymene, etc., and especially of oil of turpentine or oil of cumin.

Benzene-tricarboxylic Acids, $C_6H_3(COOH)_3$.—Three isomers are known: trimesic acid, obtained by the oxidation of mesitylene; trimellitic acid, obtained by the oxidation of colophony; and hemimellitic acid.

Benzene-tetracarboxylic Acids, $C_6H_2(COOH)_4$.—Of this formula are pyromellitic acid, prehnitic acid, and mellophanic acid.

Benzene-pentacarboxylic Acid, $C_6H(COOH)_5$.—But one acid of this formula is possible and it has been obtained.

Benzene-hexacarboxylic Acid, $C_6(COOH)_6$.—The aluminum

benzoic acid is $C_7H_6O_2$, while salicylic (oxybenzoic
$C_7H_6O_3$. In them there is at least one OH group att
rectly to the benzene nucleus, and giving to the comp
phenol character, while at the same time they contain
boxyl group COOH, and act as acids. These phenol
form with bases two classes of salts, in one of which th
acid group alone is replaced by metal, and in the other
the H of the phenol group is also replaced. Thus, we
salicylic acid both $C_6H_4\left\{\begin{matrix}OH\\COONa\end{matrix}\right.$ (neutral sodium
and $C_6H_4\left\{\begin{matrix}ONa\\COONa\end{matrix}\right.$ (basic sodium salicylate). The fi
not acted upon by carbonic acid, the second, like the
phenol, is decomposed in aqueous solution by CO_2, anc
into the first compound.

Oxybenzoic Acids, $C_6H_4\left\{\begin{matrix}OH\\COOH\end{matrix}\right.$.—Of the three is
most important is the ortho acid, which is **Acidum**
cum, U. S. P. This is found in the blossoms of *Spiræ*
and as methyl ester in oils of wintergreen and birch.
tained by the oxidation of saligenin (see p. 716), and
coumarin, indigo, ortho-cresol, etc., with caustic potas
thetically it is now made by the process of Kolbe as
by Schmidt; acting upon sodium-phenol with CO_2
vessels at a temperature of 130°:

$$C_6H_5ONa + CO_2 = C_6H_5{-}O{-}COONa.$$
$$C_6H_5{-}O{-}COONa = C_6H_4(OH)COONa.$$

There is formed in this case at first an ether-like c
sodium-phenol carbonate, and this then by molecular r
ment passes into sodium salicylate. At a somewhat hi
perature only half the phenol used is converted into
acid, the basic sodium salt is formed, and the other h
phenol distils off unchanged.

Salicylic acid crystallizes in fine needles, fusing at 1
and volatile in a current of steam. It is difficultly solub
water, more readily soluble in hot water, easily soluble
form, alcohol, and ether. Ferric chloride produces a vi
in its aqueous solutions.

The salts of salicylic acid which are official are **Lithi**
las, U. S. P., and **Sodii Salicylas, U. S. P.**

Of the esters of salicylic acid, two are official: **Met**
cylas, U. S. P., the artificial or synthetic methyl salicy

and similar substances on boiling these with sulphuric acid from their decay. It is also found in human urine in cases acute phosphorus poisoning. It has also been made synthetical from phenyl-acetaldehyde.

Isomeric with several of these monobasic phenol acids are several alcohol acids in which we have alcoholic OH in one side-chain and the carboxyl group COOH in another.

Mandelic Acid (Phenyl-glycollic Acid), $C_6H_5.CH(OH).COOH$, results upon heating amygdalin with hydrochloric acid, and is made synthetically by saponifying benzaldehyde cyanhydrin, $C_6H_5.COH.HCN$. Mandelic acid is interesting as entering into the formation of the artificial alkaloid homatropine (see Alkaloids).

Tropic Acid, $C_6H_5.CH\left\{\begin{matrix}CH_2OH\\COOH\end{matrix}\right.$, is formed by the breaking up of atropine and hyoscyamine under the influence of baryta water, the products being tropic acid, $C_9H_{10}O_3$, and tropine, $C_8H_{15}NO$. Tropic acid has also been made synthetically. Prolonged boiling with baryta water changes it into atropic acid (see p. 723).

Protocatechuic Acid, $C_6H_3(OH)_2COOH$, contains two phenol OH groups and the one COOH group. It is obtained by fusing various resins, such as catechu, benzoïn, dragon's blood, asafœtida, and others, with potash. It may be prepared synthetically by heating pyrocatechin with carbonate of ammonia. It forms lustrous needles, melting at 199°, soluble in warm water and alcohol, insoluble in benzene. It reduces ammoniacal silver solution but not Fehling's solution. The solution is colored green by ferric chloride, turning to blue after addition of Na_2CO_3. Putrefactive decomposition changes it into pyrocatechin, $C_6H_4(OH)_2$, and CO_2.

Vanillic Acid, $C_6H_3\left\{\begin{matrix}OH\\OCH_3\end{matrix}\right\}COOH$, is the monomethyl ether of protocatechuic acid. It results from the oxidation of vanillin or coniferin. Forms needles, melting at 207°, and capable of subliming.

Veratric Acid, $C_6H_3(OCH_3)_2.COOH$, is the dimethyl ether. It occurs in sabadilla seeds (*Veratrum sabadilla*). A homologue of protocatechuic acid is *orsellinic acid*, $C_6H_2(CH_3)(OH)_2COOH$, which is found in many lichens, both free and as an ester, erythrin (see p. 581).

Gallic Acid, $C_6H_2(OH)_3COOH$ (**Acidum Gallicum**, U. S. P.), is found naturally in nutgalls, in tea, in sumac, and in othe plants, and is made synthetically by several reactions. It can readily be prepared from the tannin of nutgalls by the action of dilute acids or by the change due to mould growths. It forms silky needles, fusing at 220° to 240°, and is soluble in hot water, alcohol, and ether. Is decomposed by dry distillation into pyrogallol and carbon dioxide: $C_6H_2(OH)_3COOH = C_6H_3(OH)_3 + CO_2$.

It reduces Fehling's solution, is colored blue-black with ferric chloride, but is not precipitated by lead acetate. With potassium cyanide it gives a red color, and with iodine in the presence of inorganic salts a purplish-red color.

Among the salts of gallic acid may be mentioned the *basic bismuth gallate* (or subgallate), $C_6H_2(OH)_3COOBi(OH)_2$. This compound, discovered in 1841 by Bley, has recently been brought forward as a substitute for iodoform in skin diseases, under the name of "dermatol." It forms a saffron-yellow powder, insoluble in water, alcohol, or ether, but soluble in dilute acids.

Closely related to gallic acid and occurring with it in the several natural sources mentioned is an alteration product of it:

Gallotannic Acid (Digallic Acid), $C_{14}H_{10}O_9$ (**Acidum Tannicum,** U. S. P.).—It is found in gall-nuts to the amount of 60–65 per cent., as well as in sumac, tea, etc. It is best prepared by extracting powdered nutgalls with commercial ether or with acetone. It is a light-yellowish, amorphous powder, or in scales or spongy masses, nearly odorless, and with a strongly astringent taste. It is soluble in water, difficultly soluble in absolute alcohol, and insoluble in absolute ether, benzene, and carbon disulphide. When boiled with dilute acids or alkalies, it takes up a molecule of water and yields 2 molecules of gallic acid. The aqueous solution is colored dark blue by ferric chloride. Tannin has an affinity for the animal hide and for gelatin, and is abstracted from its solution by these substances, the product in the former case being leather.

The salts of tannic acid, or the tannates, are amorphous. The iron salt is the basis of the "nutgall ink," the ferric tannate being kept in suspension by the addition of some gum to the aqueous liquid.

Gallotannic acid is but one of a large series of related tannins which are named according to their sources. The classification adopted by one of the authors in another work[*] is as follows:

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[*] The Tannins, by Henry Trimble, vol. ii. p. 132, J. B. Lippincott Co., 1894.

Group *a*. Gallotannic acid, Chestnut-wood tannin, Chestnut-bark tannin, Pomegranate-bark tannin, and Sumac tannin.

Group *b*. Oak-bark tannin, Mangrove tannin, Canaigre tannin, Rhatany tannin, Kino tannin, Catechu tannin, Tormentil tannin.

In addition to these, not classified may be mentioned Moritannic acid (from *Morus tinctoria*), Caffe-tannic acid (in coffee), Cinchona tannic acid (in cinchona bark), etc. It has been supposed that a number of these exist in the plants as glucosides, and only show the distinctive characters on the breaking up of this original combination, but all recent investigations indicate that there is no chemical combination of the tannin with glucose.

Quinic Acid, $C_6H.H_6(OH)_4COOH$, is a hexahydro-tetroxybenzoic acid. It is found in quinine bark, in coffee beans, and meadow hay. Forms prismatic crystals, fusing at 161.6°, and soluble in water. When oxidized, yields quinone and hydroquinone, and fused with caustic potash yields protocatechuic acid. The action of reducing agents converts it into benzoic acid:

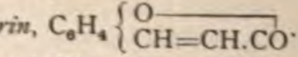
$$C_7H_{12}O_6 + H_2 = C_7H_6O_2 + 4H_2O.$$

5. Unsaturated Phenol Acids.—These acids, like the unsaturated alcohols and aldehydes, contain an unsaturated side-group with a COOH, and at the same time one or more phenol groups OH.

Coumaric Acid (Oxycinnamic Acid), $C_6H_4(OH).CH{=}CH.COOH$.—The ortho-coumaric acid is found in sweet clover (*Melilotus officinalis*), and is made synthetically by several reactions, the most interesting of which is the condensation of salicylaldehyde with acetic anhydride in the presence of acetate of soda:

$$C_6H_4(OH)CHO + (CH_3CO)_2O = C_6H_4(OH)CH{=}CH.COOH + C_2H_4O_2.$$

It forms needles melting at 207°–208°, and subliming when heated. The acid very readily loses a molecule of water and yields the anhydride

Coumarin,  $C_6H_4\left\{\begin{array}{l}O\text{———}\\CH{=}CH.CO\end{array}\right.$. It is found in Tonka beans (the seeds of *Dipterix odorata*), in woodruff (*Asperula odorata*), and other vegetable sources. It may be formed by the synthesi given above for coumaric acid, and in small quantity when malic acid is heated with phenol and sulphuric acid. Forms shinin prisms, melting at 67° and boiling at 290°. It is powerfully aro-matic, and is employed in perfumery and to impart an aroma t certain wines. It is scarcely soluble in cold water, but soluble in hot water, alcohol, and ether.

Caffeïc Acid (Dioxycinnamic Acid), $C_6H_3(OH)_2CH{=}CH.COOH$, is obtained by the decomposition of the caffe-tannic acid of coffee beans. It may also be formed synthetically by the condensation of protocatechuic aldehyde with acetic anhydride.

Ferulaïc Acid is the methyl derivative of caffeïc acid. It is found in asafœtida, and may be made synthetically from vanillin (methyl-protocatechuic aldehyde) and acetic anhydride.

Umbellic Acid is an isomer of caffeïc acid. Its anhydride is *umbelliferon*, which bears the same relation to this acid that coumarin does to coumaric acid.

Anhydrides of trioxy-cinnamic acids, or, as they may also be termed, dioxy-coumarins, are *Aesculetin* and *Daphnetin*, the products of the decomposition of the glucosides Aesculin and Daphnin.

CHAPTER VII.

AROMATIC COMPOUNDS WITH MORE THAN ONE NUCLEUS.

Two classes are here to be distinguished: compounds in whic the several benzene nuclei are joined together without condensation, and compounds in which two or more benzene nuclei hav condensed together to form a new and distinctive nucleus or grouping.

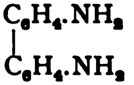
I. Compounds with Uncondensed Nuclei.

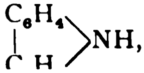
1. Diphenyl Group.—Just as the action of sodium on methyl iodide in ethereal solution by withdrawing the iodine causes the two methyl groups to unite to form ethane, $CH_3—CH_3$, so the action of sodium on brom-benzene in ethereal solution causes the two phenyl groups to unite to form

Diphenyl, $C_6H_5.C_6H_5$.—It is also formed when the vapor of benzene or benzoic acid is led through a red-hot tube, and is contained in coal-tar. White, lustrous scales, fusing at 71° and boiling at 254°. When oxidized it yields benzoic acid.

The usual replacing groups OH, NO_2, NH_2, HSO_3, and CH_3 may replace hydrogen in the diphenyl formula, and isomeric compounds are formed according to the position of the replacing group.

Among the most important of the diphenyl derivatives may be mentioned

Di-p-amido-diphenyl (Benzidine),  $\begin{array}{l}C_6H_4.NH_2\\|\\C_6H_4.NH_2\end{array}$. It is obtained by reducing the corresponding nitro compound of diphenyl. It is a diatomic base which crystallizes in colorless, silky plates, readily soluble in hot water and alcohol, and melting at 122°. It is of great importance in the color industry, since its diazo compounds react with phenols and amines to form a valuable class of dyes, which are used on cotton without previous mordanting. These are known collectively as "benzidine dyes."

Carbazole,  $\left.\begin{array}{l}C_6H_4\\|\\C_6H_4\end{array}\right>NH$, is the imide of diphenyl. It is co tained in coal-tar and in crude anthracene, and may be obtained also by passing diphenylamine (see p. 699) through red-hot tubes.

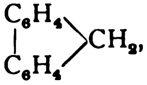
Hexoxy-diphenyl, $C_{12}H_4(OH)_6$, which dissolves in potash with violet-blue color, is the mother-substance of *Cærulignone* (or Cedriret), $C_{16}H_{16}O_6$, a violet-colored compound which is formed when crude pyroligneous acid is purified with chromate of potash, and also from the oxidation of the dimethyl-pyrogallol of beech-wood tar. It crystallizes in fine, steel-gray needles, soluble in concentrated sulphuric acid with fine blue color.

2. Diphenyl-methane Group.—The replacement of one hydrogen in methane by phenyl C_6H_5 gives us phenyl-methane, which we have already considered as methyl-benzene, or toluene; the replacement of two or three hydrogen atoms by phenyl groups gives us diphenyl-methane and triphenyl-methane compounds, which, therefore, bear a simple relation to toluene. Thus, we have

$C\begin{cases} H \\ H \\ H \\ H \end{cases}$,	$C\begin{cases} C_6H_5 \\ H \\ H \\ H \end{cases}$,	$C\begin{cases} C_6H_5 \\ C_6H_5 \\ H \\ H \end{cases}$,	$C\begin{cases} C_6H_5 \\ C_6H_5 \\ C_6H_5 \\ H \end{cases}$.
Methane.	Phenyl-methane, or toluene.	Diphenyl-methane.	Triphenyl-methane.

Diphenyl-methane, $C_6H_5.CH_2.C_6H_5$, is obtained by the action of benzyl chloride upon benzene in the presence of aluminum chloride or zinc-dust. It forms long, colorless needles, which smell of oranges. Fusing point 26°–27°.

Benzophenone (Diphenyl-ketone), $C_6H_5.CO.C_6H_5$, may be obtained by oxidizing diphenyl-methane with chromic acid, or more simply by distilling benzoic acid with lime. This reaction shows it to be the counterpart of acetone obtained by distilling acetate of lime. Colorless crystals, insoluble in water, soluble in alcohol. It is dimorphous and may crystallize in rhombic prisms, fusing at 49°, or in rhombohedra, fusing at 27°.

Fluorene (Diphenylene-methane)  $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>CH_2$, is contained in coal-tar, and crystallizes in colorless plates with a violet fluorescence. It melts at 113° and boils at 295°.

3. Triphenyl-methane Group.—Triphenyl-methane, $CH(C_6H_5)_3$, and its homologues, diphenyl-tolyl-methane,

$$CH\begin{cases} C_6H_5 \\ C_6H_5 \\ C_6H_4.CH_3 \end{cases}, \text{ and phenyl-ditolyl-methane, } CH\begin{cases} C_6H_5 \\ C_6H_4.CH_3, \\ C_6H_4.CH_3 \end{cases}$$

are of especial importance as being the mother-substances of the great majority of the so-called "aniline dyes."

Triphenyl-methane can be made synthetically by a variety of reactions. Thus, by the action of benzal chloride on benzene in the presence of Al_2Cl_6 we have

$$C_6H_5.CHCl_2 + 2C_6H_6 = CH(C_6H_5)_3 + 3HCl,$$

or from chloroform and benzene in the presence of aluminum chloride

$$CHCl_3 + 3C_6H_6 = CH(C_6H_5)_3 + 3HCl.$$

It forms white, prismatic crystals, soluble in hot alcohol and ether, fusing at 92.5° and boiling at 359°.

Triphenyl-carbinol, $(C_6H_5)_3.C(OH)$, may be prepared by oxidizing triphenyl-methane with chromic acid.

Fuming nitric acid acting upon triphenyl-methane produces *trinitro-triphenyl-methane*, $(C_6H_4.NO_2)_3CH$, and this oxidized gives *trinitro-triphenyl-carbinol*, $(C_6H_4NO_2)_3.C(OH)$. The corresponding amido compounds $(C_6H_4NH_2)_3CH$ and $(C_6H_4NH_2)_3$-$C(OH)$ are known as "para-leucaniline" and "para-rosaniline" respectively, and are the starting-points of the aniline-color manufacture.

TRIPHENYL-METHANE DYE-COLORS.

From triphenyl-methane may be derived the four groups of dye-colors which follow, and these, which, in distinction from the nitro dye-colors, the azo dye-colors, or the naphthalene and anthracene dye-colors, are called the triphenyl-methane colors, are the "aniline colors" in the narrower sense of the word. These groups are:

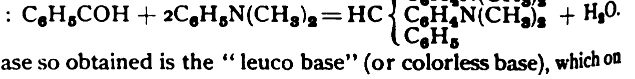
(*a*) The Malachite Green group (Diamido derivatives of Triphenyl methane).

(*b*) The Rosaniline group (Triamido derivatives of Triphenyl-methane).

(*c*) The Rosolic Acid group (Oxy derivatives of Triphenyl-methane).

(*d*) The Phthaleïn group (derivatives of Triphenyl-methane-carboxylic acid).

a. **The Malachite Green Group.**—In the presence of zinc chloride or hydrochloric acid, one molecule of benzaldehyde reacts with two molecules of dimethyl-aniline to form a tetramethylated diamido-triphenylmethane:



$$C_6H_5COH + 2C_6H_5N(CH_3)_2 = HC\begin{cases} C_6H_4N(CH_3)_2 \\ C_6H_4N(CH_3)_2 \\ C_6H_5 \end{cases} + H_2O.$$

This base so obtained is the "leuco base" (or colorless base), which on oxidation yields the color base of the dye "malachite green." The commercial dye-stuff is the chlorhydrate or zinc chloride double salt of this base. The same dye-color is also known as "Victoria green," or "bitter-almond-oil green." Homologous compounds in this group are the colors "brilliant green," "Helvetia green," and "light green," the last two containing sulphonic groups.

b. **The Rosaniline Group.**—The rosaniline dyes are derived partly from triphenyl-methane and partly from diphenyl-tolyl-methane; in the former case they are often designated as para compounds, as "para-rosaniline," because prepared from aniline and para-toluidine.

$$\textit{Para-leucaniline},\ HC\left\{\begin{array}{l}C_6H_4NH_2\\ C_6H_4NH_2\text{, and}\\ C_6H_4NH_2\end{array}\right.$$

$$\textit{Leucaniline},\ HC\left\{\begin{array}{l}C_6H_3(CH_3)NH_2\\ C_6H_4NH_2\text{,}\\ C_6H_4NH_2\end{array}\right.$$

result from the reduction of the corresponding trinitro compounds. The free leuco bases crystallize in colorless needles or plates, melting at 148° and 100° respectively. When these bases or the commercial mixture (aniline oil) containing them are oxidized, we obtain *para-rosaniline*,

$$(OH)C\left\{\begin{array}{l}C_6H_4NH_2\\ C_6H_4NH_2\text{, and } \textit{rosaniline},\\ C_6H_4NH_2\end{array}\right.\ (OH)C\left\{\begin{array}{l}C_6H_3(CH_3)NH_2\\ C_6H_4NH_2\\ C_6H_4NH_2\end{array}\right. .$$

These color bases unite with acids to form the actual dye-stuffs. Thus, *Fuchsine* (or Aniline Red, Magenta, etc.) is the chlorhydrate of rosaniline, and its formation takes place with the elimination of water, as shown:

$$(OH)C\left\{\begin{array}{l}C_6H_3(CH_3)NH_2\\ C_6H_4NH_2\\ C_6H_4{\cdot}NH_2\end{array}\right. + HCl = C\left\{\begin{array}{l}C_6H_3(CH_3)NH_2\\ C_6H_4NH_2\\ C_6H_4NH{\cdot}HCl\end{array}\right. + H_2O.$$

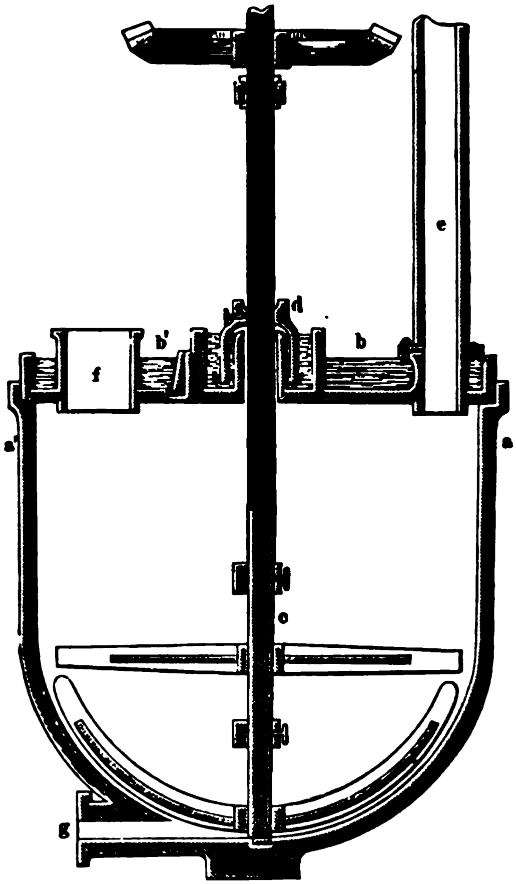
The several stages in the practical manufacture of magenta may be outlined as follows: The commercial benzene is a mixture of benzene and toluene. This is nitrated, the process being carried out on a large scale in a series of vessels of the construction shown in Fig. 103. The product after thorough washing is a mixture of nitro-benzene with ortho- and para-nitro-toluene. This is now to be reduced to commercial aniline, which is accomplished in a still of the construction shown in Fig. 104, the reducing agent being nascent hydrogen generated by a mixture of iron filings and hydrochloric acid. The reaction once started usually develops sufficient heat not only to carry it to completion, but to distil over part of the aniline. This is then finished by the aid of a current of steam. The product is "aniline oil," of which several grades are designated according to the quality. "Aniline oil for reds," used in the manufacture of magenta, is a mixture of ortho- and para-toluidine with some 40 per cent. of aniline; "aniline for safranine" contains aniline and ortho-toluidine, but little or no para-toluidine; while "aniline for blues" contains almost pure aniline.

The aniline oil (mixture of leucanilines) is now to be oxidized. The agents used for this have been syrupy arsenic acid, stannic chloride, mercuric chloride or nitrate, and, lastly, nitro-benzene itself. When the oxidation is complete the acid is added to form a salt, and this is extracted and the product purified by crystallization.

The crystals of magenta, while dissolving with strong red color, appear in compact form a lustrous metallic green, although the powder is reddish.

Acid Magenta is essentially rosaniline trisulphonate of sodium. I
logues of magenta, or *methylated rosanilines*, are obtained by the r
ment of the hydrogen atoms of the amido groups by methyl. Eth
phenyl groups also act in the same way.

FIG. 103.



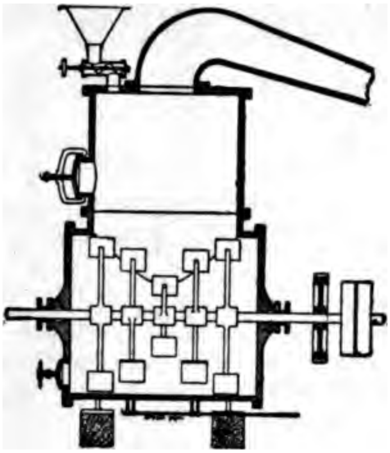
Manufacture of nitro-benzene.

Methyl Violet is a mixture of the hydrochlorates of penta- and
methyl-*p*-rosaniline. The red shade of the para-rosaniline salts is c
into violet by the entrance of methyl or ethyl groups, the intensity
shade increasing with the number of the groups. This methyl vio
been introduced into medicine under the name of "pyoktanin,
recommended as an antiseptic, especially in eye-clinics and practic

Hofmann's Violet is a mixture of methylated and ethylated rosa
or rather their chlorhydrates and iodohydrates.

Phenylated Rosanilines.—By the entrance of phenyl groups into the rosaniline molecule the violet color which first results soon changes to a blue, when three phenyl groups have entered. Hence *Aniline Blue* is triphenyl-rosaniline hydrochloride. It is a beautiful blue dye, soluble in alcohol, but insoluble in water. It is, therefore, often known as "spirit blue." It is made soluble in water by the process of sulphonating, and thus are obtained the dyes known as "alkali blue," "water blue," etc.

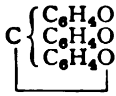
FIG. 104.



Aniline still.

c. **The Rosolic Acid Group.**—Just as aniline may be changed into phenol by diazotizing and boiling with water (see p. 705), so para-rosaniline and aniline may be changed into corresponding compounds in which, instead of amido groups, we have phenol OH groups. Thus, to

$$\underset{\text{Para-rosaniline.}}{(OH)C\left\{\begin{array}{l}C_6H_4NH_2\\C_6H_4NH_2\\C_6H_4NH_2\end{array}\right.}\quad \text{correspond}\quad (OH)C\left\{\begin{array}{l}C_6H_4OH\\C_6H_4OH\\C_6H_4OH\end{array}\right.\quad \text{and}$$

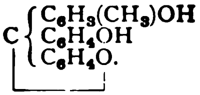


$$C\left\{\begin{array}{l}C_6H_4OH\\C_6H_4OH,\\C_6H_4O\end{array}\right.$$

Aurin.

$$\text{and to}\quad \underset{\text{Rosaniline.}}{(OH)C\left\{\begin{array}{l}C_6H_3(CH_3)NH_2\\C_6H_4NH_2\\C_6H_4NH_2\end{array}\right.}\quad \text{correspond}\quad (OH)C\left\{\begin{array}{l}C_6H_3(CH_3)OH\\C_6H_4OH\\C_6H_4OH\end{array}\right.$$

and



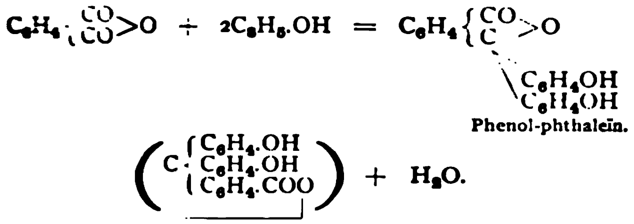
$$C\left\{\begin{array}{l}C_6H_3(CH_3)OH\\C_6H_4OH\\C_6H_4O.\end{array}\right.$$

Rosolic Acid.

The dyes here obtained, aurin and rosolic acid, are, it will be seen, anhydrides of the carbinols first obtained. They differ, moreover, from rosaniline and *p*-rosaniline, in being acid dyes and not basic.

Among the other dyes of this class are the yellow and the red corallin. The dyes of this class have not any present importance.

3. The Phthalein Group.—The phthaleïns result from the action of one molecule of phthalic anhydride (see p. 722) upon two molecules of a phenol with the separation of water. Thus:



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}O + 2C_6H_5.OH = C_6H_4\left\{\begin{matrix}CO\\C\end{matrix}\right.{>}O \begin{matrix}\diagdown C_6H_4OH\\ \diagdown C_6H_4OH\end{matrix}$$

Phenol-phthaleïn.

$$\left(C\left\{\begin{matrix}C_6H_4.OH\\C_6H_4.OH\\C_6H_4.COO\end{matrix}\right.\right) + H_2O.$$

In this case we see that the loss of the elements of water causes the phthalic anhydride and the two molecules of phenol to unite to form a new compound, the phthalein. It may be written as first shown to illustrate its formation from phthalic anhydride, but the other method shows its character as a triphenyl-methane derivative.

Phenol-phthaleïn forms colorless needles, fusing at 250°–253°, which are insoluble in water, soluble in alcohol. Alkalies also dissolve it with red color, which the slightest excess of acid causes to disappear. Hence its use as an indicator in alkalimetry. (**Phenol-phthalein Test-solution** U. S. P.)

Resorcin-phthaleïn (Fluorescein) is formed by heating phthalic anhydride with resorcin to 200°. Dark, reddish-yellow crystals, difficultly soluble in alcohol. Dissolves in alkalies to a yellowish-red solution, fluorescing green. The sodium salt of fluorescein is known as "Uranine," and is used for dyeing wool yellow.

Eosin is the potassium salt of tetrabrom-fluorescein. Its aqueous solution shows a reddish-yellow color and yellowish-green fluorescence. It is extensively used for dyeing silks and woollens.

By using chlorinated, brominated, and other substituted phthalic acids, a considerable number of modified Eosins are obtained, like *Erythrosin*, *Rose de Bengale*, *Primrose*, *Phloxin*, etc., all of which show fluorescence. *Rhodamine* is a similar red dye of beautiful fluorescing properties.

Gallein is the phthalein of Pyrogallol. It dissolves in alkalies with blue color, and with red color in alcohol. Zinc-dust reduces it to *gallin*, which is dissolved by sulphuric acid, yielding *Cœruleïn*, a dye dissolving in alkalies with green color and used as a green dye.

4. The Indigo Group.—In the Indigo plant (*Indigofera tinctoria*), as well as in woad (*Isatis tinctoria*) and other plants, is present a glucoside, *Indican*, which by its decomposition, which takes place by a spontaneous fermentation when the plant is cut, dissolved in the dilute acid solution. Its sodium salt comes into commerce as "Indigo-carmine," or soluble indigo-color.

Isatin, $C_8H_5NO_2$ $\left(\text{or } C_6H_4\left\langle\begin{smallmatrix}CO\\N\end{smallmatrix}\right\rangle C(OH)\right)$, is formed by the oxidation of indigo with nitric acid. It forms yellowish-red prisms, soluble in hot water and alcohol, fusing at 200°-201°. When dissolved in excess of concentrated sulphuric acid, it gives a blue color with thiophene, or benzene containing thiophene (see Thiophene, p. 675).

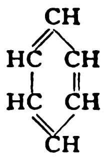
By reduction of isatin are obtained ***dioxindol***, ***oxindol***, and ***indol***.

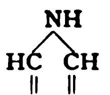
Indoxyl, $C_8H_7NO\left(\text{or } C_6H_4\left\langle\begin{smallmatrix}C(OH)\\NH\end{smallmatrix}\right\rangle CH\right)$, is found in the form of its sulphonic acid in normal urine in small amount and under pathological conditions (stoppage of the intestine) in larger amount. Yields indigo when oxidized. Indoxyl may be tested for in the urine by adding strong hydrochloric acid and a few drops of chlorinated soda as an oxidizing agent, when the blue color of indigo will be obtained.

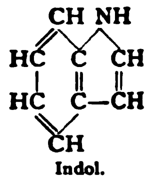
The underlying substance of the whole indigo group is

Indol, $C_6H_4\left\langle\begin{smallmatrix}CH\\NH\end{smallmatrix}\right\rangle CH$.—This substance is obtained readily from albuminoids by the action of bacteria, by the pancreatic fermentation, and by fusion with caustic potash. It has also been made synthetically by heating *o*-nitrocinnamic acid with potash and iron filings, by heating aniline with monochloracetaldehyde, and by other reactions. It forms lustrous white leaflets, melting at 52° and readily volatile with steam. It has the peculiar odor of fæces.

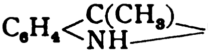
Indol can be considered as the condensation product of a benzene nucleus and a pyrrol nucleus, as illustrated by the structural formulas:


Benzene.


Pyrrol.


Indol.

In this formula, two carbon atoms are common to both the benzene and the pyrrol nuclei. We shall have examples of similar condensation of two or more benzene nuclei in the formulas of naphthalene and anthracene.

Skatol (β-methylindol),  $C_6H_4{<}\genfrac{}{}{0pt}{}{C(CH_3)}{NH}{>}CH$, is found in the fæces, and is formed from albumen by fusion with potash or by the action of bacteria, generally accompanied by indol. It may also be made synthetically from propionaldehyde and phenylhydrazine. It forms white, lustrous leaflets, melting at 95° and boiling at 265°–266°, and possessing a strong odor of fæces. A pine chip, moistened with an alcoholic skatol solution and then dipped in cold, strong hydrochloric acid, is colored first cherry-red and then dark violet.

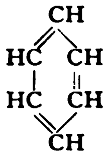
II. COMPOUNDS WITH TWO CONDENSED BENZENE NUCLEI.

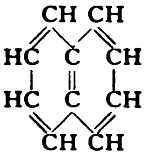
In the higher-boiling portions of coal-tar occur hydrocarbons still richer relatively in carbon than benzene,—that is, containing relatively less hydrogen for a given number of carbon atoms. While the general formula of benzene and its homologues was C_nH_{2n-6}, these hydrocarbons belong mainly in two series, possessing the general formulas C_nH_{2n-12} and C_nH_{2n-18} respectively. These hydrocarbons not only belong to the closed-chain or cyclic hydrocarbons, but they bear a close relationship to benzene, and are, in fact, derivatives of it. This is seen, for instance, in the fact that naphthalene, the representative of the formula C_nH_{2n-12}, when oxidized yields phthalic acid, and anthracene, the representative of the formula C_nH_{2n-18}, when oxidized yields benzoic acid.

1. Naphthalene Series. (General formula C_nH_{2n-12}.)

Naphthalene, $C_{10}H_8$ (**Naphtalinum,** U. S. P.), is a product of destructive distillation of many organic compounds, being formed when ethylene, acetylene, alcohol, ether, acetic acid, camphor, etc., are decomposed by heat, as in passing through a red-hot tube. Is mainly extracted from coal-tar, of which it is an abundant constituent. It forms white, lustrous scales, melting at 79.2° and boiling at 218°, but volatile in a current of steam. Is insoluble in water, soluble in hot alcohol and in ether. Naphthalene has a strong and characteristic coal-tar odor. It is used as an antiseptic and disinfectant, and as a substitute for camphor as a preservative against moths (hence the designation "coal-tar camphor"), and on a large scale for the manufacture of phthalic acid and numerous derivatives used in the dye-color industry, and for carburetting illuminating gas.

The constitution of naphthalene has been established by a study of its decompositions and is illustrated by the following graphic formulas:

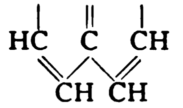

Benzene.

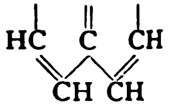

Naphthalene.

In this formula, two benzene nuclei are considered to have condensed, two atoms of carbon being held in common by the two parts which have united. This gives us 10 atoms of carbon, of which only 8, however, are free to attach hydrogen, hence the formula $C_{10}H_8$.

2. Addition Compounds of Naphthalene.—Naphthalene takes up hydrogen far more readily than benzene does, and forms first *naphthalene dihydride*, $C_{10}H_8.H_2$, and *naphthalene tetrahydride*, $C_{10}H_8.H_4$. By more intense action of hydriodic acid and phosphorus the second benzene nucleus is also attacked, and a *hexahydride*, $C_{10}H_8.H_6$, and finally a *dekahydride*, $C_{10}H_8.H_{10}$, are formed. It also yields chlorine addition products more readily than benzene does, such as *naphthalene dichloride*, $C_{10}H_8.Cl_2$, and *naphthalene tetrachloride*, $C_{10}H_8.Cl_4$. This latter is manufactured on a large scale by the action of potassium chlorate and hydrochloric acid upon naphthalene, and is then oxidized by the aid of nitric acid, yielding phthalic acid as product (see p. 722).

3. Substitution Derivatives of Naphthalene.—In speaking of benzene it was stated (see p. 681) that in the case of mono-substitution compounds it mattered not which H atom of the benzene molecule was considered to have been replaced. In the case of naphthalene we find that there are two mono-chlornaphthalenes, two mono-nitronaphthalenes, etc. The reason of this is apparent on examining the structural formula of naphthalene. It will be seen that in the accompanying two cases represented the replacement in the one formula is of a hydrogen attached to a carbon adjacent to one of the two linking carbons, and in the other formula is of a hydrogen not adjacent to either of these linking carbon atoms:





β-Naphthol (**Naphtol,** U. S. P.).—Fuming sulphuric acid acting upon naphthalene at 80°–90° produces α-naphthalene-sulphonic acid chiefly, but at 200° β-naphthalene-sulphonic acid is the chief product. The sodium salt of this acid is fused with caustic soda, and the result is β-naphthol-sodium. From this the official compound is liberated by the addition of hydrochloric acid. It forms colorless, silky scales or crystalline powder of a weak phenol-like odor and sharp taste. It fuses at 123° and boils at 286°. Alkalies produce a bluish-violet fluorescence; ferric chloride produces a greenish color. β-naphthol is soluble in alcohol, ether, benzene, chloroform, oils, and alkalies.

It is quite analogous in chemical properties to phenol or carbolic acid. It is largely used for external application as an antiseptic; taken internally it is a poison. β-naphthol should be free from contamination with α-naphthol, as this is quite poisonous. The ferric chloride test above mentioned serves to distinguish them ; with α-naphthol a violet color is obtained.

Two derivatives of β-naphthol have been introduced into medicine :

β-Naphthyl-salicylate (Betol), $C_6H_4(OH)COOC_{10}H_7$.—This compound is the counterpart of salol, which is phenyl salicylate. It forms a pure white powder of lustrous crystals, melting at 95°. It is difficultly soluble in both cold and hot water, easily soluble in boiling alcohol, ether, benzene, and warm linseed oil. Its therapeutic action is almost the same as that of salol, decomposing in the intestine into salicyclic acid and β-naphthol. The other derivative is

β-Naphthol-α-monosulphonate of Calcium (Asaprol).—It has been recommended for internal administration in cases of rheumatism, gout, etc.

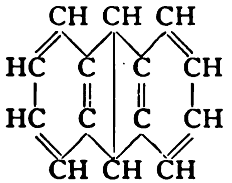
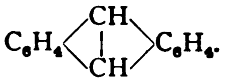
Dioxynaphthalenes, $C_{10}H_6(OH)_2$, the counterparts of the diatomic phenols, are also known. Similarly corresponding to quinone, $C_6H_4O_2$, are the α- and *β-naphthoquinones*, $C_{10}H_6O_2$. These are produced directly by the oxidation of naphthalene with chromic acid.

Both the hydroxyl group, OH, and the quinone group, O_2, may exist in the same molecule. We have an *oxynaphthoquinone*, $C_{10}H_5(OH)O_2$, and a *dioxynaphthoquinone*, $C_{10}H_4(OH)_2O_2$. This latter is known as "naphthazarine" (or alizarine black), a valuable dye-color.

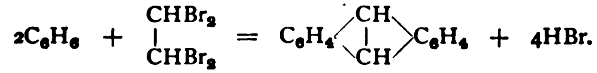
Homologues of naphthalene, such as α- and *β-methyl-naphthalenes*, are found in coal-tar. From these are derived the *naphthoic* *acids*, $C_{10}H_7.COOH$, just as benzoic acid is derived from toluene or methyl-benzene, and corresponding to the oxybenzoic acids (such as salicylic acid) we have *α*- and *β-oxynaphthoic acids*. Of these the former has been used in medicine as an antiseptic of very similar character to salicylic acid.

III. Compounds with Three Condensed Nuclei.

Under the general formula C_nH_{2n-18} we have two hydrocarbons of the composition $C_{14}H_{10}$, besides homologues of these. These hydrocarbons are anthracene and phenanthrene, and both occur in coal-tar.

1. **Anthracene and its Derivatives.**—Anthracene is a product of destructive distillation of organic material, such as coal-tar, petroleum, turpentine oil, etc., and can be made synthetically from a variety of sources. Its structural formula is considered to be , in which formula we have two benzene residues C_6H_4 united by the group C_2H_2 as the middle nucleus. This group, C_2H_2, with the equivalence four, links together the two parts in the manner expressed by the full structural formula given above, or sometimes expressed  $C_6H_4\left\langle\begin{matrix}CH\\|\\CH\end{matrix}\right\rangle C_6H_4$.

That the two OH groups which join together the two benzene nuclei are also linked with each other by a single bond is indicated by several reactions, among which may be mentioned the formation of anthracene from benzene and tetrabromethane in the presence of aluminum chloride:



$$2C_6H_6 + \begin{matrix}CHBr_2\\|\\CHBr_2\end{matrix} = C_6H_4\left\langle\begin{matrix}CH\\|\\CH\end{matrix}\right\rangle C_6H_4 + 4HBr.$$

It is obtained from the fraction of the coal-tar boiling above 300° and known as the "green oil" (or anthracene oil) by chilling this and pressing out the crude anthracene in cakes of greenish-yellow color. The pure hydrocarbon forms colorless plates of white color with blue fluorescence. It fuses at 213° and boils above 360°. With picric acid it forms an addition compound, crystallizing in beautiful red needles. It is difficulty soluble in alcohol and ether, readily soluble in hot benzene or toluene. When oxidized it yields ***anthraquinone***, while reducing agents change it to ***anthracenehydride***, $C_6H_4<\genfrac{}{}{0pt}{}{CH_2}{CH_2}>C_6H_4$, and on prolonged action to ***anthracene hexahydride***, $C_{14}H_{16}$, and ultimately to ***anthracene perhydride***, $C_{14}H_{24}$.

The chief uses of anthracene are in the preparation of alizarine and similar artificial dye-colors.

Anthraquinone, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_4$, is readily obtained by the oxidation of anthracene by chromic acid in glacial acetic acid and by the distillation of calcium benzoate :

$$(C_6H_5.COO)_2Ca = C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_4 + CaO + H_2O.$$

It forms yellow prisms, soluble in hot benzene or glacial acetic acid, fusing at 277°, and boiling at over 360°. By distillation in contact with zinc-dust it yields anthracene again. Fused at high temperatures with caustic potash it yields benzoic acid. By heating with strong sulphuric acid it is made to yield sulphonic acids, such as ***anthraquinone-monosulphonic acid***, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_3(HSO_3)$, and ***anthraquinone-disulphonic acids***, $C_{14}H_6(HSO_3)_2O_2$. These sulphonic acids are of great technical importance as being steps in the synthetic formation of alizarine.

Oxyanthraquinones are formed when hydrogen of the anthraquinone formula is replaced by OH groups. Thus, ***mono-oxyanthraquinone*** is $C_{14}H_7(OH)O_2$, and ***dioxyanthraquinone*** is $C_{14}H_6\cdot(OH)_2O_2$. Of this latter there are a number of isomers, of which the most important is alizarine. *Trioxyanthraquinones*, $C_{14}H_5\cdot(OH)_3O_2$, are also obtained, of which anthragallol and purpurine are the most important. The methods for the formation of these very important technical compounds will be noted later.

Alizarine (Ortho-dioxyanthraquinone), $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_2\cdot(OH)_2$, is found in madder-root (***Rubia tinctorum***), where it results from the decomposition of a glucoside, rubianic acid (ruberythric acid). It has been known from early historic times, and was used in the East for the cotton and damask dyeing known as "Turkey red."

Since 1867, when Graebe and Liebermann first effected its synthesis from anthracene, it has been made artificially in a variety of ways. Thus, the first synthesis was from anthracene, by the action of bromine upon the anthraquinone, and then fusing the dibromanthraquinone with caustic potash, as shown:

$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_4 + 4Br = C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_2Br_2 + 2HBr.$$

$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_2Br_2 + 2KOH = C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_2(OH)_2 + 2KBr.$$

This first synthesis was soon superseded by that involving the use of fuming sulphuric acid. The mono- and disulphonic acids when fused with caustic alkali should yield by theory the corresponding oxyanthraquinones. It is found, however, in practice, that oxygen is always absorbed from the air, and that the monosulphonic acid when fused yields a mixture of mono- and di-oxyanthraquinones, and the disulphonic acid yields a mixture of di- and tri-oxyanthraquinones. Chlorate of potash is, therefore, added in practice to facilitate their partial oxidation and to complete the change. The reactions then for the manufacture of alizarine are:

$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_3(HSO_3) + NaOH = C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_3(OH) + NaHSO_3.$$

$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_3(OH) + O = C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_2(OH)_2.$$

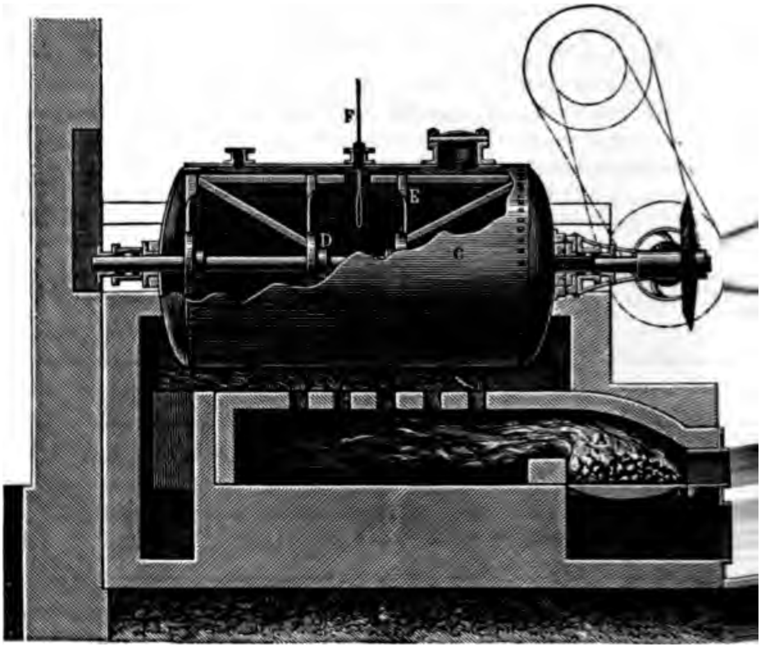
Of course as an excess of the fused alkali is present, the alizarine, as formed, becomes sodium alizarate, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_2(ONa)_2$, which is soluble in water with rich purple color. From this solution, on addition of hydrochloric acid, the alizarine is precipitated as a tawny-yellow powder, which generally comes into commerce in the moist state as a 10-per-cent. or 20-per-cent. paste.

The fusion of the anthraquinone sulphonate with the caustic alkali is carried out at a temperature of 180° to 200° in an autoclave provided with mechanical agitation, as shown in Fig. 105. If the anthraquinone-disulphonic acid is taken for the fusion with caustic alkali, the product is mainly a mixture of isomeric trioxy-anthraquinones.

Alizarine crystallizes in fine red prisms or needles, which melt at 282°, and can be sublimed. It is readily soluble in alcohol and ether, combines with a violet or purple color with alkalies, and forms various colored insoluble compounds or "lakes" with metallic oxides, the ones of chief importance being those of aluminum and tin (red), the iron (violet-black), and the lime (reddish-blue). The finest color obtained with alizarine, known as "Turkey red," is produced by mordanting the materials with acetate of alumina and treating them with a sulphonated castor oil, known as "Turkey red oil," before applying the alizarine.

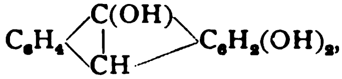
Derivatives of Alizarine.—By the action of nitrogen tetroxide upon alizarine is formed ***β-nitro-alizarine***, or "alizarine orange," $C_{14}H_7(NO_2)O_4$, used as a dye. By heating this compound wi glycerin and sulphuric acid is formed ***alizarine blue***, $C_{17}H_9NO$ It is brought into commerce as a colorless combination of the dy color with sodium bisulphite, which is printed upon the goods an

FIG. 105.



Manufacture of alizarine.

then steamed, when the alizarine-blue color is deposited upon th fibre. By the reduction of alizarine with ammonia and zinc-dus is formed ***desoxyalizarine***,



$$C_6H_4\left\langle\begin{array}{c}C(OH)\\|\\CH\end{array}\right\rangle C_6H_2(OH)_2,$$

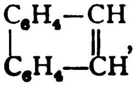
which under the name of "anthrarobin," has been used in medicine a non-poisonous substitute for chrysarobin and chrysophanic acid.

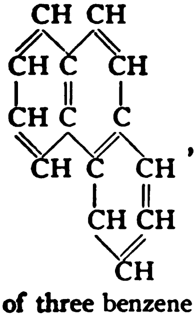
Purpurine (Trioxyanthroquinone), $C_{14}H_5(OH)_3O_2$.—This dye is found along with alizarine in madder-root, and is also prepared artificially. *Flavopurpurine* and *anthrapurpurine* are isomers formed in the fusion of anthraquinone-disulphonic acid with alkali. *Anthragallol* is also an isomer, which comes into commerce as "alizarine brown."

A homologue of anthracene is also found in coal-tar,—viz., *Methyl-anthracene*, $C_{14}H_9(CH_3)$. It is capable of analogous reactions, yielding a quinone and hydroxyl derivatives of the same. The name of one of the latter is *Chrysophanic Acid* (Dioxy-methyl-anthraquinone), $C_{14}H_5(CH_3)(OH)_2O_2$. It is found in certain lichens, in yellow dock (*Rumex*), in senna, and in rhubarb. It crystallizes in golden-yellow prisms or needles, melting at 102°, and soluble in alcohol, ether, or benzene. Alkalies also dissolve it, forming dark-red solutions. When distilled over zinc-dust it yields methyl-anthracene.

Chrysarobin, U. S. P., which is found in Goa and araroba powder, has the formula $C_{30}H_{26}O_7$, and bears the same relation to chrysophanic acid that anthrarobin does to alizarine. It readily yields chrysophanic acid by its oxidation. It forms yellow scales or neédles, melting at 170°–178°, is insoluble in water and ammonia, soluble in alkalies, with yellow color which gradually turns red, as on exposure to the air chrysophanic acid is formed. It is used like anthrarobin for external application in skin diseases.

Emodin (Trioxy-methyl-anthraquinone), $C_{15}H_{10}O_5$, occurs with chrysophanic acid in the bark of wild cherry and in rhubarb-root. When distilled with zinc-dust it also yields methyl-anthracene. It forms orange-red crystals, melting at 245°–250°.

2. Phenanthrene, $C_{14}H_{10}$, is an isomer of anthracene, and is also found in coal-tar. Its structural formula differs from that of anthracene, and is represented as  $\begin{array}{l} C_6H_4-CH \\ \vert \qquad\ \ \Vert \\ C_6H_4-CH \end{array}$, or more fully



, in which formula is shown the condensation of three benzene nuclei, the middle one having two carbon atoms jointly with each of the side nuclei. It crystallizes in colorless, lustrous scales, melting at 99° and boiling at 340°. It may be separated from anthracene by fractional distillation, followed by repeated crystallization from alcohol, in which it is much more soluble than anthracene. It forms a crystalline compound with picric acid, crystallizing from benzene in yellow needles, melting at 145°, and soluble in hot alcohol without decomposition.

Phenanthrenquinone, $C_{14}H_8O_2$, is obtained by oxidizing phenanthrene by chromic acid mixture. It crystallizes in dark orange-yellow prisms, melting at 198°. When ignited with soda-lime it yields diphenyl, $(C_6H_5)_2$, in almost the theoretical proportions, whereas anthraquinone gives benzene when similarly treated.

The phenanthrene molecule is contained in the alkaloid morphine, as when this latter is distilled with zinc-dust phenanthrene is obtained.

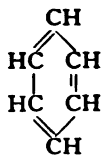
IV. COMPOUNDS CONTAINING NITROGEN IN THE BENZENE NUCLEUS.

By the replacement of one triad group, CH, in the benzene molecule by the element nitrogen we obtain *Pyridine*, C_5H_5N.

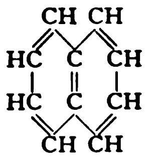
By the replacement of one triad group, CH, in the naphthalene molecule by the element nitrogen we obtain *Quinoline*, C_9H_7N.

By the replacement of one triad group, CH, in the anthracene molecule by the element nitrogen we obtain *Acridine*, $C_{13}H_9N$.

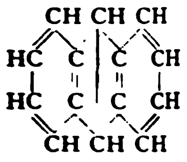
The relations of these nitrogenous bases to the parent hydrocarbons is shown clearly by a comparison of the graphic formulas:



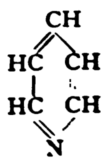
Benzene.



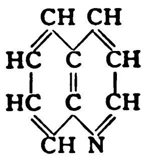
Naphthalene.



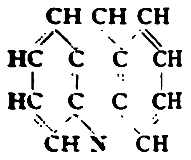
Anthracene.



Pyridine.



Quinoline.



Acridine.

1. Pyridine Bases.—Pyridine, C_5H_5N, and several of its homologues are found in coal-tar and in the animal oils (Dippel's oil) obtained by the distillation of bones. They are also found in the products of the distillation of bituminous shales. Except that they are strong bases, they bear a great analogy to the aromatic hydrocarbons, and give rise to similar derivatives. Thus, It is a strong base, throwing the hydrates of aluminum, chromium, and iron out of the solutions of the salts of these metals. It has been used in medicine as a remedy for asthma.

By the action of metallic sodium pyridine is polymerized, forming *dipyridine*, $C_{10}H_{10}N_2$, together with a compound analogous to diphenyl (see p. 730), known as *dipyridyl*, $C_{10}H_8N_2$.

Methyl-pyridines, $C_5H_4(CH_3)N$.—The three isomeric methylpyridines, known also as "picolines," are found in coal-tar. The β-compound may also be prepared from acroleïn-ammonia, or from strychnine, by distilling with lime. Liquids of unpleasant, penetrating odor.

Ethyl- and *Propyl-pyridines* are both known. The latter, we shall see, bears a close relation to the natural alkaloid conine. Thus, conyrine, $C_8H_{11}N$, which is obtained on heating conine with zinc-dust, and which yields conine again when treated with HI, is α-normal-propyl-pyridine.

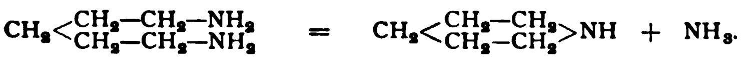
Dimethyl-pyridines, $C_5H_3(CH_3)_2N$.—In bone-oil and tar-oil three isomeric compounds of this formula, known also as "lutidines," have been found.

Trimethyl-pyridines, $C_5H_2(CH_3)_3N$. — These compounds, known as "collidines," are found in bone-oil and obtained from cinchonine by heating with potash.

Pyridine-carboxylic Acids.—While pyridine itself is quite stable and resists the action of oxidizing agents, its homologues, like those of benzene, are very readily oxidized, yielding the corresponding carboxylic acids. Three mono-carboxylic acids, $C_5H_4N.COOH$, are known,—viz., α acid—*picolinic acid*, melting at 135° ; β acid—*nicotinic acid*, melting at 231° ; and γ acid—*isonicotinic acid*, melting at 309°. These acids may be obtained by the oxidation of the α-, β-, and γ-picolines respectively with potassium permanganate. The β acid is also obtained by the oxidation of the alkaloid nicotine by different oxidizing agents. On heating with lime the above acids yield pyridine, just as benzoic acid yields benzene under similar conditions.

Of the six possible di-carboxylic acids, $C_5H_3N.(COOH)_2$, all are known. The only ones requiring mention are *quinolinic acid*, obtained by the oxidation of quinoline and *cinchomeronic acid*, the chief product of the oxidation of quinine by nitric acid, as well as from cinchonine along with other products. Of the pyridine-tricarboxylic acid, $C_5H_2N(COOH)_3$, two may also be mentioned : *hydroxycinchomeronic acid*, obtained from quinine, quinidine, and cinchonidine by boiling with an alkaline solution of potassium permanganate, and ***berberonic acid***, obtained from berberine when oxidized by nitric acids.

Hydrogen-addition Products of Pyridine.—Just as benzene, C_6H_6, is capable of taking up six hydrogen atoms and yielding hexahydrobenzene, $C_6H_6.H_6$, so pyridine may take up six hydrogen atoms and yield hexahydropyridine or ***piperidine***, $C_5H_5N.H_6$. This compound, in addition to being produced synthetically, as above mentioned, is obtained by the decomposition of the alkaloid piperin of pepper, which, under the influence of alcoholic potash, splits into piperidine and piperic acid. An important synthesis of piperidine is also that from pentamethylene-diamine, as shown:



$$CH_2<\begin{matrix}CH_2-CH_2-NH_2\\CH_2-CH_2-NH_2\end{matrix} \quad = \quad CH_2<\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}>NH \quad + \quad NH_3.$$

Pentamethylene-diamine = Piperidine + Ammonia.

Piperidine is a colorless liquid, boiling at 106°, easily soluble in water and alcohol, and of a peculiar peppery odor. It is a strong base, and forms crystallized salts.

Two of the natural alkaloids may be mentioned here, as they are hydrogen-addition derivatives of pyridine.

Conine, $C_8H_{17}N$, is *dextro-rotatory α-normal propyl-piperidine*, $C_5H_{10}N(C_3H_7)$. This is the poisonous principle of the hemlock (*Conium maculatum*), and is found chiefly in the seeds. Colorless liquid, of stupefying odor, boiling at 166°. Easily soluble in ether and alcohol, more difficultly in water. It has been made synthetically by Ladenburg from α-allyl-pyridine, which, reduced by sodium in alcoholic solution, yields an optically inactive, normal propyl-piperidine, and this by the crystallization of its tartrate is split into a dextro-rotatory variety (the true conine) and a lævo-rotatory variety. Hydrogen iodide reduces it at a high heat to normal octane, C_8H_{18}, while nitric acid oxidizes it to butyric acid.

Piperidine, as well as conine, can be methylated, and the products are known as methyl-piperidine and methyl-conine. The latter is also found in the hemlock with conine.

Nicotine, $C_{10}H_{14}N_2$, the alkaloid of tobacco, is *hexahydro-dipyridyl*, $C_{10}H_8(H_6)N_2$. It exists in the tobacco plant combined with malic and citric acids. Pure nicotine is a colorless, oily liquid, turning brown in the air; soluble in water, alcohol, and ether, of stupefying odor, and boiling at 250° with decomposition. It is intensely poisonous. When oxidized yields nicotinic (β-pyridine-carboxylic) acid, and by loss of hydrogen dipyridyl, $(C_5H_4N)_2$.

Tropine, the decomposition product of the alkaloids Atropine and Hyoscyamine, is also a hydrogenated pyridine derivative.

Cocaine and *Ecgonine*, its decomposition product, are similarly derivatives of these hydrogenated pyridines.

2. **Quinoline Bases.**—By the dry distillation of organic substances, such as bituminous coal and bones, is produced a series of bases known by this name. The same bases are also obtained in the distillation of quinine and cinchonine with potash. A number of synthetic methods have also been found for their preparation, of which may be mentioned:

(*a*) By heating acroleïn-aniline quinoline is formed, just as the heating of acroleïn-ammonia yields pyridine.

(*b*) By the oxidation of allylaniline with heated oxide of lead:

$$C_6H_5.NH(C_3H_5) + O_2 = C_9H_7N + 2H_2O.$$

(*c*) By heating aniline with glycerin, concentrated sulphuric acid, and nitrobenzene. This method (discovered by Skraup) is that now employed for the manufacture of quinoline. 24 parts of nitrobenzene, 38 parts of aniline, 120 parts of glycerin, and 100 parts of concentrated sulphuric acid are taken and heated, at first carefully, and then for several hours with inverted condenser. The mixture is now diluted with water, and the nitrobenzene distilled off. Caustic soda is then added to strong alkaline reaction, and the quinoline distilled off in a current of steam. In this reaction the sulphuric acid first dehydrates the glycerin, producing acroleïn, which then unites with the aniline to form the quinoline molecule with the elimination of hydrogen. The nitrobenzene furnishes the oxygen to combine with this hydrogen, and is itself reduced to aniline. The reactions may be summarized thus:

$$2C_6H_5.NH_2 + C_6H_5.NO_2 + 3C_3H_8O_3 = 3C_9H_7N + 11H_2O.$$

By using the homologues of acroleïn in the first of these methods instead of acroleïn we obtain the homologues of quinoline, as methyl-quinoline (quinaldine), dimethyl-quinoline, etc.

The constitution of the quinoline molecule has already been referred to and illustrated. That it contains the benzene nucleus is shown by its syntheses from aniline and nitrobenzene; that it contains a pyridine nucleus joined with this is shown by the fact that, when oxidized by potassium permanganate, quinoline yields pyridine-dicarboxylic (cinchomeronic) acid.

Quinoline, C_9H_7N, is a pale-yellowish liquid with considerable refractive power and a characteristic aromatic odor. It boils at 237°, and has a specific gravity of 1.084. Only slightly soluble in water, easily soluble in alcohol, ether, chloroform, and petroleum benzene. It is darkened in color on exposure to light. It is a base, and forms a series of crystallizable and deliquescent salts. Among these may be mentioned:

Quinoline Hydrochlorate, $C_9H_7N.HCl$, forms a colorless, deliquescent salt, easily soluble in water, with a biting and sharp taste.

Quinoline Tartrate, $3C_9H_7N.4(C_4H_6O_6)$. — This salt forms white, rhombic needles, which have a slight odor of bitter-almond oil, and taste sharp and peppermint-like. It is permanent in air, and fuses at 125°. It is moderately soluble in water, more difficultly soluble in alcohol, and almost insoluble in ether. It is extensively used in medicine as an antiseptic and antipyretic.

Quinoline Salicylate, $C_9H_7N.C_7H_6O_3$, forms a whitish, crystalline powder, not very soluble in water, easily soluble in alcohol, ether, benzene, vaseline, fats, and glycerin. It is used in medicine as the tartrate, and in similar amounts.

Homologues of Quinoline. — The methyl group may replace H in either the benzene nucleus or the pyridine nucleus of the quinoline molecule. The compounds so obtained are isomeric. Thus, the compound obtained by the replacement of a hydrogen atom of the pyridine nucleus by methyl is known as *quinaldine*, and is found in coal-tar. When oxidized by chromic acid it yields quinoline-carboxylic acid. On the other hand, the compound obtained by the replacement of a hydrogen atom of the benzene nucleus by methyl is known as *Toluquinoline*, and has only been obtained synthetically. When oxidized it yields pyridine-dicarboxylic acid. By heating quinaldine with phthalic anhydride and chloride of zinc is obtained a phthaleïn of the composition $C_6H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\}CH.C_9H_6N$. It is known as "quinoline yellow," and is insoluble in water, and difficultly soluble in alcohol. On sulphonation with fuming sulphuric acid is obtained a disulphonic acid, the sodium salt of which is known as "soluble quinoline yellow."

Oxy-quinolines.—Those derivatives which have the OH group replacing hydrogen of the benzene nucleus have a phenol-like character, and unite with diazo salts to form azo dye-colors. On the other hand, those oxy-quinolines which contain the OH group in the pyridine nucleus are called *carbostyriles.*

Hydrogen Addition Compounds.—Nascent hydrogen from tin and hydrochloric acid produces *dihydro-quinoline*, C_9H_9N, melting at 161°, and a liquid *tetrahydro-quinoline*, $C_9H_{11}N$, boiling at 245°. By the action of methyl iodide upon this latter is obtained *methyl-tetrahydro-quinoline*, the acid sulphate of which was introduced into medicine as an artificial febrifuge under the name of "kairoline."

Similarly, the oxy-quinoline before mentioned is converted by the action of tin and hydrochloric acid into *oxy-tetrahydro-quinoline*, and by the action of either methyl or ethyl iodide upon this were obtained bases of febrifuge power. The hydrochlorate of ethyl-oxytetrahydro-quinoline was known as "kairine A," and that of methyl-oxytetrahydro-quinoline as "kairine M." They were, perhaps, the first of the artificial febrifuges, but are no longer in use, being accompanied by injurious after-effects.

Isomeric with the methyl-oxytetrahydro-quinoline, $C_9H_9(OH)\text{-}N.CH_3$, is the base *tetrahydro-paraquinanisol*, $C_9H_{10}(OCH_3)N$, the sulphate and tartrate of which have been introduced into medicine under the name of "thalline," because of the emerald-green color produced in its solution by ferric chloride. It is used as an antipyretic, antiseptic, and antifermentative.

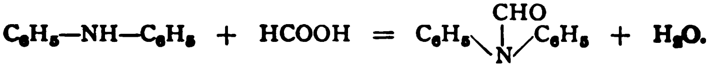
Other quinoline derivatives that have been proposed for use in medicine are "diaphtherine," a compound of one molecule of orthophenol-sulphonic acid (aseptol) with two molecules of ortho-oxy-quinoline; "analgene," *ethyoxy-ana-monobenzoyl-amido-quinoline*, $C_9H_5(OC_2H_5).NH.COC_6H_5.N$, recommended as a febrifuge and antineuralgic; and "orexine," the chlorhydrate of phenyldihydro-quinazoline, $C_{14}H_{12}N_2.HCl + 2H_2O$, which has been recommended as a stomachic and stimulant to digestion.

Quinoline-carboxylic Acids.—Among the mono-carboxylic acids of the formula $C_9H_6N.COOH$ may be mentioned *quinaldinic acid*, obtained by oxidizing quinaldine and *cinchoninic acid*, obtained by oxidizing cinchonine with potassium permanganate or nitric acid. When distilled with lime it yields quinoline.

Kynurenic Acid is an oxy-quinoline-carboxylic acid. It occurs in the urine of dogs. *Quininic Acid*, $C_9H_5(OCH_3)N.COOH$, is the methyl-phenol ether of another oxy-quinoline-carboxylic acid. It is obtained by oxidizing quinine and quinidine with chromic acid in sulphuric acid solution. Quinoline-dicarboxylic acids, $C_9H_5N(COOH)_2$, are also known.

3. **Acridine and its Derivatives.**—Acridine, $C_{13}H_9N$, has already been explained and its relationship to anthracene stated (see p. [illegible]). It is found in coal-tar and in the crude anthracene

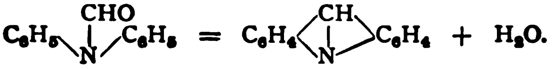
extracted therefrom. It has been made synthetically from diphenylamine, formic acid, and zinc chloride :



$$C_6H_5{-}NH{-}C_6H_5 + HCOOH = C_6H_5{\diagdown}\underset{N}{\overset{CHO}{|}}{\diagup}C_6H_5 + H_2O.$$

Diphenylamine + Formic Acid = Formyl-diphenylamine.

This compound then breaks up into acridine and water :



$$C_6H_5{\diagdown}\underset{N}{\overset{CHO}{|}}{\diagup}C_6H_5 = C_6H_4\left\langle\begin{matrix}CH\\|\\N\end{matrix}\right\rangle C_6H_4 + H_2O.$$

Acridine.

It forms colorless needles or scales, fusing at 107°–111°. Scarcely soluble in water, easily soluble in ether, alcohol, benzene, carbon disulphide, etc. It is a base, and dissolves in dilute acid with a beautiful green fluorescence. Acridine irritates the skin and mucous membranes, whence the name. Among its derivatives are several important dye-colors, such as *chrysaniline*, which is the nitrate of diamido-phenylacridine, and *benzoflavine*, which is an isomer of the other.

CHAPTER VIII.

THE ALKALOIDS AND PTOMAINES.

THE term alkaloid has been applied to a number of physiologically active principles occurring in the vegetable kingdom, and this common occurrence was emphasized more than any general chemical character. It is true it was recognized that they were nitrogenous, and that they acted as derived ammonias in their method of forming salts, but for a long time nothing more definite could be said with regard to their chemical nature. It is now recognized that, while the great majority of these are derivatives of the basic compounds pyridine and quinoline, just noticed in the preceding pages, there are also methane derivatives among them, as caffeine and theobromine, which are related to uric acid, and that, besides the occurrence of these important bases in the plant kingdom, substances answering to many of the alkaloid tests are produced in the decay of animal tissue, giving rise to the so-called "cadaveric alkaloids," or ptomaïnes. It remains true of all these classes, however, that we have to do with derived ammonias, either amines or amides, and this feature, together with their physiological activity, must be taken to constitute the basis of their claim to the name alkaloid, whether synthetically formed, as conine now can be, or found in the vegetable or animal kingdom only. The termination *ine* has been made uniform for them as expressing their basic character and their derivation from ammonia.

Classification of the Alkaloids.—Leaving the animal alkaloids for subsequent consideration, we find that the vegetable alkaloids may be divided into two classes: those which are liquid and volatile, and those which are solid and non-volatile. At the same time we find that with this physical distinction corresponds a difference in chemical composition,—viz., the liquid alkaloids do not contain oxygen, while the solid alkaloids are oxygenated bases. As the liquid alkaloids are very limited in number, no further grouping is necessary for them. For the solid alkaloids it has been found convenient to group them in addition according to the order or family of plants in which related alkaloids are soda is then treated with ammonium chloride, and shaken with amyl alcohol in order to extract morphine. The solution containing ammonium chloride is evaporated and extracted with strong alcohol, which may yield solanine, berberine, etc. This method of Stas and Otto was next modified by Rodgers and Girdwood, who employed chloroform instead of ether, and by Uslar and Erdmann, who recommended the use of amyl alcohol.

2. **Method of Dragendorff.**—This method is the most comprehensive one as yet proposed, and is in most general use. It is given in outline: The material to be investigated is extracted with dilute sulphuric acid. The extract which contains the alkaloids as sulphate is evaporated and precipitated with alcohol. It is then filtered and the alcoholic filtrate evaporated. The acid solution is then extracted in succession with petroleum ether, benzene, and chloroform. The portion undissolved is made alkaline with ammonia and then extracted in succession with petroleum ether, benzene, chloroform, and amyl alcohol. Seven extractions are thus made, which may be tabulated as follows:

I. Extractions from acid solutions:
  - (*a*) With petroleum ether: piperine, and, in addition, carbolic, salicylic, and picric acids.
  - (*b*) With benzene: cantharidin and digitalin, berberine and colchicine.
  - (*c*) With chloroform: narcotine, picrotoxin, and digitaleïn.

II. Extractions from alkaline solutions:
  - (*a*) With petroleum ether: nicotine, conine, quinine, and some strychnine.
  - (*b*) With benzene: quinine, atropine, cocaïne, strychnine, brucine, veratrine, and thebaïne.
  - (*c*) With chloroform: a little morphine, papaverine.
  - (*d*) With amyl alcohol: morphine, solanine, narceïne.

3. **Sonnenschein's Method.**—In this method the material is acidified with dilute hydrochloric acid, and then phosphomolybdic acid is added, which precipitates all the alkaloids. The precipitate is warmed with baryta water, when the volatile alkaloids may be distilled off. The solution, after filtering off the barium precipitates, is freed from barium by addition of carbon dioxide, and the aqueous solution is then investigated by the methods of either Stas-Otto or Dragendorff. The objection to this method is that the treatment with barium hydrate may cause decomposition in some of the active principles present.

4. Method of Brieger.—This is chie
the ptomaïnes if present in a suspected
treated with hydrochloric acid to convert
and then, after a preliminary clarifying
sary, with lead acetate, the ptomaïnes ar
curic chloride solution. Most of these b
(tetanine is an exception), and, after su
water and freeing it from mercury by
ptomaïnes are obtained in the form of do
platinic chlorides, and tested by experim

The special description of the more i
now be taken up on the basis of the sin
made.

VOLATILE ALKALO

As the simplest of the naturally occu
mentioned *methylamine* and *trimethyla*
found at times in the vegetable kingdom
ucts of decomposition of animal tissue
been noted and their varied occurrence d

Piperidine, $C_5H_5N.H_6$, has been foun
pepper as a decomposition-product of pi
been described under the name of hex
751).

Conine, $C_8H_{17}N$ (or $C_5H_{10}(C_3H_7)N$).–
ferred to as α-normal-propyl-piperidine,
rotatory variety of the same, having bee
Ladenburg.

Conine is the poisonous alkaloid of the
ulatum), and is an oily liquid of a pecul
colorless when freshly prepared, but be
mately resinoid on keeping. It is solubl
water, and is readily dissolved by alcoho
hol, ether, chloroform, petroleum ether,
strong base and neutralizes acids perfe
of conine with chromic-acid mixture, nor
duced. The reaction may be employed
butyric acid is readily recognized by its o

Associated with conine in the conium
important bases: *Conhydrine*, $C_8H_{17}N$
isomeric with the former; *methylconin*
piperidine, $C_7H_{15}N$.

Conine is an extremely powerful paralytic poison, which acts on the motor nerves; one drop is a distinctly poisonous dose, while ten drops may be fatal.

Nicotine, $C_{10}H_{14}N_2$.—This alkaloid has been referred to and stated to be hexa-hydro-dipyridyl. It is the poisonous principle of tobacco, in which it exists combined with malic and citric acids in amounts ranging from about 1 per cent. to 7 per cent. of the dry leaf. The nicotine is a colorless, oily liquid of sp. gr. 1.011 at 15°, which on prolonged exposure to air becomes yellow and ultimately resinous. It has a strong and unpleasant odor, recalling that of tobacco, a sharp, caustic taste, and is intensely poisonous. It is soluble in water and alcohol, but is extracted from its aqueous, alkaline solutions by agitation with ether, chloroform, benzene, amyl alcohol, or petroleum naphtha. Nicotine is precipitated by Mayer's reagent from very dilute solutions. On adding mercuric chloride to a solution of nicotine, a white, crystalline precipitate is produced, soluble in dilute hydrochloric or acetic acid. This is the most characteristic reaction of nicotine. From conine, nicotine is distinguished by its odor, by being heavier instead of lighter than water, and by its reactions with mercuric chloride, platinic chloride (yellowish, crystalline precipitate), and picric acid (yellow, amorphous precipitate turning crystalline). The poisonous effects of tobacco when taken into the stomach, it is agreed, are entirely due to the nicotine. When tobacco is smoked, the greater part of the nicotine is converted into pyridine and other decomposition-products; some, however, escapes decomposition, as Melsens has proved the presence of unchanged nicotine in tobacco smoke in a proportion equal to about one-seventh of that present in the original tobacco. Vohl and Eulenberg have concluded from their experiments that the intense action of tobacco smoke on the nervous system is not due to nicotine at all, but to the presence of the bases of the pyridine series.

Piturine, $C_{12}H_{16}N_2$.—The volatile alkaloid of pituri (the dried leaves of *Duboisia Hopwoodii*, a shrub growing in Australia was regarded by Petit as identical with nicotine, but its individual character was established by Liversidge. In chemical characters and physiological effects it bears a close resemblance to nicotine, but can be distinguished by gently warming it with hydrochloric acid. Nicotine so heated turns violet, while piturine does not change at all.

Lobeline is the active principle of *Lobelia inflata*, or Indian tobacco. Paschkis and Smita obtained the alkaloid as a viscous oil with an odor at once resembling honey and tobacco.

Sparteine, $C_{15}H_{26}N_2$, is obtained from the
and branches of broom (*Spartium scopariu*
liquid, boiling at 287°. It has a somewhat pun
very bitter taste, and on exposure to air turn
soluble in alcohol, ether, and chloroform, bu
ether. When oxidized with potassium perma
acid, together with a non-volatile, pyridine-carb
with lime yields pyridine.

Spigeline is the active principle of *Spigeli*
root." It was obtained as a volatile alkaloid
milk of lime.

NON-VOLATILE ALKAL

1. The Belladonna Alkaloid Grou
alkaloids exist in the plants of the famil
been named atropine and belladonine,
donna, hyoscyamine and hyoscine, from
supposed daturine, from *Datura stram*
from *Duboisia myoporoïdes*, have been
with atropine and hyoscyamine respective
are distinguished by a remarkable powe
and hence are often termed the "mydriati
bases, atropine, hyoscyamine, and hyos
isomeric, and hyoscyamine, it is found,
pine by prolonged heating above its fusin
of alkalies.

Atropine (Daturine), $C_{17}H_{23}NO_3$, **Atro**
to the class of tropeïnes, or compound
$C_8H_{15}NO$. When the natural alkaloid
chloric acid or baryta water, it is decompo
ing to the reaction :

$$\underset{\text{Atropine.}}{C_{17}H_{23}NO_3} + H_2O = \underset{\text{Tropine.}}{C_8H_{15}N}$$

The preferable method of effecting the
alkaloids is to heat the alkaloid with sa
60° or 80° for a few hours. When the
an acid, especially concentrated hydrochlo
loses the elements of water, and atropi
On the other hand, the tropic acid and tr
hydrolysis of either atropine or hyoscya
gether at 100° with dilute hydrochloric ac

Pure atropine forms white, acicular
having a bitter, acrid taste, and gradually

2. The Cinchona Alkaloids.—The barks of the *Cinchona Calisaya*, *Cinchona officinalis*, and of hybrids of these, are, according to the U. S. Pharmacopœia, the sources of quinine and its associated alkaloids, containing not less than 5 per cent. of total alkaloids, of which 2.5 per cent. is quinine. The maximum percentage of quinine seems to have been reached in the *Cinchona Ledgeriana*, grown in Java in 1876, which yielded 13.25 per cent. of quinine. These barks contain some 32 natural alkaloids, and in the processes of extraction and purification some 8 additional bases are formed by alteration of the naturally occurring ones.

The list of naturally occurring cinchona alkaloids, as given by A. H. Allen, on the authority of Paul and Cownley, is as follows:

I. *Cinchonine class:*
  Paricine, $C_{16}H_{18}N_2O$.
  Cinchotine, $C_{19}H_{24}N_2O$.
  Cinchonamine, "
  Hydrocinchonine, "
  Hydrocinchonidine, "
  Cinchonine, $C_{19}H_{22}N_2O$.
  Cinchonidine, "
  Homocinchonidine, "
  Cinchonicine, "
  Paytine, $C_{21}H_{24}N_2O$.
  Paytamine, "

II. *Quinamine class:*
  Quinamine, $C_{19}H_{24}N_2O_2$.
  Conquinamine, "
  Javanine, ——.
  Cupreine, $C_{19}H_{22}N_2O_2$.

III. *Quinine class:*
  Hydroquinine, $C_{20}H_{26}N_2O_2$.
  Hydroquinidine, "
  Quinine, $C_{20}H_{24}N_2O_2$.
  Quinidine, "
  Quinicine, "

IV. *Cusconine class:*
  Chairamine, $C_{22}H_{26}N_2O_4$——.
  Conchairamine, "
  Chairamidine, "
  Conchairamidine, "
  Concusconine, "
  Aricine, $C_{23}H_{26}N_2O_4$.
  Cusconine, $C_{23}H_{26}N_2O_4$.
  Cusconidine, "
  Cuscamine, ——.
  Cuscamidine, ——.

V. *Anhydro-bases:*
  Dicinchonicine, $C_{38}H_{44}N_4O$.
  Diquinicine, $C_{40}H_{46}N_4O_3$——

Of all this list, however, four stand out as more important, and all four are represented among official compounds. These four are *quinine* and *quinidine*, which are isomers with the formula $C_{20}H_{24}N_2O_2$, and *cinchonine* and *cinchonidine*, isomers with the formula $C_{19}H_{22}N_2O$.

In the free state these alkaloids are colorless or slightly yellowish solids, fusible but not volatile without decomposition. They are generally but slightly soluble in water, but more readily soluble in alcohol, and generally quite soluble in ether and chloroform. When soluble in these last two liquids, they may be

a deep-green coloration only. The thallei
given by quinidine and cupreine, but not b
isomers. It is prevented by morphine. T
ture of iodine to a solution of acid sulphate
alcohol, a compound is produced known a
composition $4C_{20}H_{24}N_2O_2, 3H_2SO_4, 2HI, I_4$
called also "iodo-sulphate of quinine," is
of similar compounds formed by the acti
sulphates of the cinchona bases. It is on
water or dilute alcohol, but is soluble in boil
cent., and is deposited on cooling in tabul
dichroic, and, as before stated, when in th
power of polarizing light. Herapathite is
nine sulphate by treatment with sulphurou
hydrogen sulphide, and other reducing ag
sulphate of quinine is much less soluble tha
compounds of the other cinchona bases,* it
by de Vrij as a basis for the determination

While the complete synthesis of quinine
effected, it has been made from the accom
preine of the *Cinchona cuprea.* When cup
hol solution is treated with metallic sodium
in a sealed tube under pressure, the foll
place :

$$C_{19}H_{23}N_2O.ONa + CH_3Cl = NaCl +$$

Cupreine-sodium.

Two basic substances isomeric with quinine ha
thetically : one, discovered by C. A. Kohn, was
hydroxy-hydroquinoline with ethylene dibromid
$C_9H_{10}(OH)N.C_2H_4.NC_9H_{10}(OH)$; the other wa
and Otto by the action of β-naphthylamine on
according to the reaction :

$$C_{10}H_7NH_2 + C_{10}H_{16}O.NOCl = HCl$$

The salts of quinine that are official at
phate, the bisulphate, the hydrobromate, th
the valerianate. With reference to the fi
necessary to note that the cinchona bases
sulphates, — viz., neutral sulphates, with

---

* The solubilities of the iodosulphates of the prin
in acidulated alcohol at 15° are as follows : Quinine he
cinchonidine herapathite, 1 in 92 parts ; quinidine h
cinchonine, 1 in 42 parts.

$R_2H_2SO_4$, and acid or bisulphates, with the formula RH_2SO_4. The former of these have a neutral reaction to litmus and methyl-orange, and are in general sparingly soluble in water, while the second class are generally readily soluble.

Quinine Sulphate, $(C_{20}H_{24}N_2O_2)_2H_2SO_4.7H_2O$ (**Quininæ Sulphas,** U.S.P.).—This, the staple salt of quinine, is generally made on a large scale direct from the cinchona barks. For its preparation the following process, differing but slightly from that given in the U. S. Pharmacopœia of 1870, may be used.

Because of the fact that the naturally occurring salts of the alkaloid, the quinate and quino-tannate, are only moderately soluble, the powdered bark is repeatedly extracted with cold water acidified with dilute sulphuric acid. The several extraction-liquors are then united, supersaturated with milk of lime, and the precipitate, consisting of the cinchona bases, the calcium salts of sulphuric, quino-tannic, quinic, and quinovic acids and other substances, is washed, pressed, and slowly but completely dried. This dry precipitate is then repeatedly boiled with strong alcohol, and the clear extraction-liquid allowed to cool to separate a portion of the difficultly soluble cinchonine. The liquid separated from these crystals is then exactly neutralized with sulphuric acid and the alcohol distilled off. On cooling, there separates out the greater part of the quinine sulphate, which is difficultly soluble in water and dilute alcohol, while the more soluble sulphates of cinchonine, cinchonidine, quinidine, quinamine, etc., with a small quantity of quinine sulphate, remain in the mother liquor. To further purify the separated quinine sulphate, after pressing, it is dissolved in boiling water, decolorized with a little bone-black, and the solution allowed to stand again to crystallize. This operation may be repeated, if necessary. The quinine sulphate remaining in the mother liquor may be recovered by evaporating the solution to dryness, decomposing the sulphate with sodium carbonate, washing the free base which separates, dissolving it in the amount of dilute sulphuric acid needed for exact neutralization, and crystallizing it out.

Instead of using ethyl alcohol for the extraction, kerosene oil has been used in England, and amyl alcohol (fusel oil) quite extensively in this country.

The official sulphate forms loose, white, needle-like crystals of a somewhat silky lustre, which, however, is easily impaired by its tendency to lose water of crystallization and effloresce superficially. It is odorless, but of a persistent, very bitter taste.

Quinine Acid Sulphate, $C_{20}H_{24}N_2O_2,H_2SO_4.7H_2O$ (**Quininæ Bisulphas,** U. S. P.), is readily formed by dissolving quinine sulphate in the calculated amount of dilute sulphuric acid. It forms colorless, transparent, rhombic crystals of a bitter taste. It is soluble in 10 parts of water, forming a solution which fluoresces strongly blue and shows acid reaction. It loses its water of crystallization at 100° C., and at 135° it melts and is converted into the isomeric quinicine bisulphate, which in dilute sulphuric acid solution has a yellow color but no blue fluorescence.

Quinine Hydrobromate, $C_{20}H_{24}N_2O_2.HBr.H_2O$ (**Quininæ Hydrobromas**, U. S. P.), forms light, white, silky needles, odorless, but with a very bitter taste. It is soluble in 54 parts of water at 15°. The salt is neutral or faintly alkaline. The aqueous solution when acidulated with sulphuric acid shows a fine blue fluorescence.

Quinine Hydrochlorate, $C_{20}H_{24}N_2O_2.HCl.2H_2O$ (**Quininæ Hydrochloras**, U. S. P.), forms white, silky, asbestos-like crystals which become anhydrous at 120°. It is soluble in 34 parts of water at 15° and in 3 parts of alcohol. The dilute, aqueous solution shows some little fluorescence, which becomes stronger on adding dilute sulphuric acid.

Quinine Valerianate, $C_{20}H_{24}N_2O_2,C_5H_{10}O_2.H_2O$ (**Quininæ Valerianas**, U. S. P.), forms colorless, triclinic plates, having a pearly lustre and a faint odor of valeric acid. It is not deliquescent. It is soluble in 100 parts of water at 15° and in 5 parts of alcohol.

Ferri et Quininæ Citras, U. S. P., and **Ferri et Quininæ Citras Solubilis**, U. S. P., are official scale preparations.

Quinidine (Conquinine), $C_{20}H_{24}N_2O_2$, is an isomer of quinine, and occurs frequently in cinchona barks. It is present to a considerable extent in commercial "quinoidine" (chinoidine). The free base crystallizes from alcohol in large, monoclinic, efflorescing needles, containing 2½ molecules of water. It gives the thalleioquin reaction like quinine and shows a blue fluorescence in dilute sulphuric-acid solution, but is dextro-rotatory and is sparingly soluble in ether, two points of difference.

Quinidine Sulphate $(C_{20}H_{24}N_2O_2)_2H_2SO_4.2H_2O$ (**Quinidinæ Sulphas**, U. S. P.), crystallizes in white, silky needles or prisms, which require 100 parts of water or 8 parts of alcohol for solution. This salt differs from the sulphates of the other cinchona alkaloids in requiring a temperature of 120° to render it anhydrous, and in readily taking up the water again in moist air.

Cinchonine, $C_{19}H_{22}N_2O$ (**Cinchonina**, U. S. P.).—This base is invariably present in cinchona barks. When the bases are crystallized from alcohol, the cinchonine, being the least soluble, deposits first. It crystallizes in anhydrous, shining prisms or needles, which melt at 165°. It is almost insoluble in cold water, requiring 3760 parts at 15° and 3500 parts at a boiling tempera-ucts. The mixed bases are boiled with hydrochloric acid, whereby they all suffer hydrolysis with formation of ecgonine; then by passing dry hydrochloric acid into a solution of ecgonine hydrochloride in methyl alcohol, the hydrochloride of ecgonine methyl-ester is formed, which, on concentrating the alcoholic solution, crystallizes out in prisms. Cocaine is formed when this compound is heated on the water-bath with an equal weight of benzoyl chloride until the mixture becomes homogeneous and the evolution of hydrochloric acid ceases. The melted mass is poured into water and separated from the insoluble benzoic acid, when the cocaine is precipitated by ammonia and recrystallized from alcohol. The artificial alkaloid possesses all the properties of the natural cocaine.

Cocaine crystallizes from alcohol in colorless, monoclinic prisms, melting at 97°–98°. It is very slightly soluble in water but readily soluble in alcohol, ether, chloroform, benzene, petroleum spirit, and carbon disulphide. Cocaine is lævo-rotatory. Its chief use in medicine is as a local anæsthetic.

Cocaine Hydrochlorate, $C_{17}H_{21}NO_4.HCl$ (**Cocainæ Hydrochloras, U. S. P.**).—It forms colorless, transparent crystals of a saline taste and producing upon the tongue a tingling sensation, followed by a numbness of some minutes' duration. It is readily soluble in water and alcohol, difficultly soluble in ether. At 19[illegible]° it melts with partial sublimation.

4. The Opium Alkaloids.—Opium contains, besides the two indifferent compounds *meconoisin*, $C_8H_{10}O_2$, and *meconin*, $C_{10}H_{10}O_4$, a series of alkaloids which occur for the most part combined with meconic acid. The complete list of the opium alkaloids thus far recognized is:

[illegible]
[illegible]
[illegible]
[illegible]
[illegible]
[illegible]
[illegible]
[illegible]
[illegible]
[illegible]

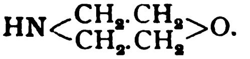
Cryptopine, $C_{21}H_{23}NO_5$
Rhœadine, $C_{21}H_{21}NO_6$
Narcotine, $C_{22}H_{23}NO_7$
Oxynarcotine, $C_{22}H_{23}NO_8$
Narceine, $C_{23}H_{29}NO_9$
Pseudomorphine, $C_{34}H_{36}N_2O_6$
Gnoscopine, $C_{34}H_{36}N_2O_{11}$
Tritopine, $C_{42}H_{54}N_2O_7$
Hydrocotamine, $C_{12}H_{15}NO_3$

[illegible] morphine is always present in opium in largest [illegible]. The amount of narcotine present [illegible] that of papaverine from 0.5 to 1 per cent., that of codeine from 0.2 to 0.8 per cent., that of thebaine from 0.2 to 0.5 per cent., and that of narceine from 0.1 to 0.4 per cent. The other bases are less important, and are found in relatively small amount. Besides these bases, opium contains some resin and caoutchouc-like bodies, fat, wax, gum, coloring matter, inorganic salts, and water.

Opium, U. S. P., is the concrete, milky exudation obtained by incising the unripe capsules of *Papaver somniferum* Linné (nat. ord. *Papaveraceæ*), yielding in its normal moist condition not less than 9 per cent. of "crystallized morphine," when assayed by the official process (see Part V., Opium Assay). The opium used for pharmaceutical purposes is mainly the Smyrna or Turkey opium, the Persian and East Indian varieties being, however, worked on a large scale for the extraction of alkaloids.

Morphine, $C_{17}H_{19}NO_3 + H_2O$ (**Morphina,** U. S. P.), forms "colorless or white, shining, prismatic crystals or fine needles or a crystalline powder, odorless, and having a bitter taste, permanent in air." It loses its water of crystallization at 120° C. It is difficultly soluble in water, somewhat more soluble in alcohol, insoluble in ether and benzene. Its aqueous solutions are lævo-rotatory.

Morphine when distilled with zinc-dust yields pyridine, quinoline, pyrrol, and phenanthrene. It is considered to be a derivative of a hydrogenized phenanthrene combined with morpholine,



$HN{<}\genfrac{}{}{0pt}{}{CH_2.CH_2}{CH_2.CH_2}{>}O$. It contains two OH groups, of which one seems to be phenolic and the other alcoholic in character. In codeine (methyl morphine) the hydrogen of the phenol OH has been replaced, and in methocodeine the hydrogen of the alcoholic OH also.

Color Reactions of Morphine.—A small fragment of a crystal of morphine tested with the following reagents will give color reactions more or less characteristic :

1. With a drop of perfectly neutral solution of ferric chloride or iron-alum is obtained a deep greenish-blue color changed to green by excess of the reagent.

2. Nitric acid (1.42 sp. gr.) will turn the fragment of morphine an orange-red color, which changes to yellow on heating, and is destroyed on adding sodium thiosulphate.

3. Morphine, when pure, yields with pure, concentrated sulphuric acid in the cold either no color or at most a faint pink color. On heating to 150°, a dirty-green (or rose-red) color is developed. On allowing it to cool and diluting with water, a greenish-blue color is produced.

4. The solution of morphine in concentrated sulphuric acid, with a little nitric acid or potassium nitrate added, gives a red coloration turning to brown.

5. Froehde's reagent (pure concentrated sulphuric acid which contains 1 mg. sodium or ammonium molybdate to the c.c.) gives with morphine a fine violet color, changing to blue and dirty green, and ultimately to pale red.

6. A mixture of morphine and cane-sugar (in proportion of 1 to 4) added to concentrated sulphuric acid will give a purple color, changing to blood-red. The addition of a drop of bromine water brings out the color more strongly.

Of the salts of morphine the following are official: **Morphinæ Acetas, U. S. P.**, $C_{17}H_{19}NO_3.C_2H_4O_2 + 3H_2O$, **Morphinæ Hydrochloras, U. S. P.**, $C_{17}H_{19}NO_3.HCl + 3H_2O$, and **Morphinæ Sulphas**, $(C_{17}H_{19}NO_3)_2H_2SO_4 + 5H_2O$.

When morphine or its hydrochlorate is heated to 140°–150° in a sealed tube with a large excess of strong hydrochloric acid, or with zinc chloride at 110°, it is converted into the hydrochlorate of *apomorphine*, the formula of which differs from that of morphine by the elements of water.

The hydrochlorate (**Apormorphinæ Hydrochloras, U. S. P.**), $C_{17}H_{17}NO_2.HCl$, forms minute grayish-white, acicular crystals, without odor, and of a faintly bitter taste, and acquiring a greenish tint on exposure to air and light. It is moderately soluble in water and alcohol, only slightly soluble in ether or chloroform. Codeine, $C_{18}H_{21}NO_3$, when treated in a similar way with hydrochloric acid, yields first $C_{18}H_{20}ClNO_2$, and then splits off methyl chloride and leaves apomorphine, $C_{17}H_{17}NO_2$.

Codeine is morphine methyl-ester, $C_{17}H_{17}NO(OH)OCH_3$, and has been made synthetically by heating morphine with methyl iodide.

Narceine, $C_{23}H_{29}NO_9$, crystallizes with $2H_2O$ in long, white prisms or needles. The anhydrous base melts, according to Merck, at 170°–171°. It has powerful hypnotic properties.

Narcotine, $C_{22}H_{23}NO_7$, crystallizes from alcohol or ether in colorless needles or prisms, melting at 170°. Above 200° it is decomposed into *meconin*, $C_{10}H_{10}O_4$, and *cotamine*, $C_{12}H_{13}NO_3.H_2O$.

Papaverine, $C_{20}H_{21}NO_4$, is a weak base of feebly narcotic properties.

Thebaine, $C_{19}H_{21}NO_3$.—It crystallizes from strong alcohol in needles, which melt at 193°. It has a sharp and styptic taste, and is a powerful tetanic poison, producing symptoms resembling those of strychnine.

talline powder or groups of prismatic needles. It is more soluble than strychnine in water, and very soluble in alcohol. Brucine is a weaker base than strychnine and is not so poisonous. When treated with concentrated sulphuric acid and oxidizing agents it does not give the color reactions seen with strychnine. On the other hand, with nitric acid of 1.42 sp. gr., brucine gives a blood red color, which on heating becomes yellowish-red and yellow.

6. Aconite Bases.—*Aconitum napellus* (monk's-hood or wolf's-bane), *Aconitum ferox*, and *A. Fischeri* (Japanese aconite) contain a number of related alkaloids which, according to C. R. Alder Wright, are esters either of benzoic acid or of a derivative of this acid. Thus, when heated with water alone, each of the *crystalline* bases undergoes saponification, with formation of benzoic acid or a derivative thereof, together with a new amorphous base which generally has far less physiological activity than the crystalline alkaloid from which it is derived.

These crystalline alkaloids, together with the products of their hydrolysis, are :

Crystalline Base.	Amorphous Base.	Acid.
Aconitine, $C_{33}H_{45}NO_{12}$ (from *A. napellus*).	Aconine, $C_{26}H_{41}NO_{11}$.	Benzoic acid, $C_7H_6O_2$.
Picraconitine, $C_{31}H_{45}NO_{10}$ (from *A. paniculatum*?).	Picraconine, $C_{24}H_{41}NO_9$.	Benzoic acid, $C_7H_6O_2$.
Japaconitine, $C_{66}H_{88}N_2O_{21}$ (from *A. Fischeri*).	Japaconine, $2C_{26}H_{41}NO_{10}$.	Benzoic acid, $2C_7H_6O_2$.
Pseudaconitine, $C_{36}H_{49}NO_{12}$ (from *A. ferox*).	Pseudaconine, $C_{27}H_{41}NO_9$.	Veratric acid (dimethyl-protocatechuic acid), $C_9H_{10}O_4$.

7. Veratrum Alkaloids.—In the *Veratrum viride* and *V. album* are contained several alkaloids which have been the subject of repeated studies. The most recent views indicate the existence of the following :

Jervine, $C_{12}H_{22}NO_2$.—Melts at 237.7° and is slightly lævorotatory.

Veratroidine (Rubijervine), $C_{32}H_{53}NO_9$.—Melts at 149.2° and is optically inactive.

Pseudojervine, $C_{29}H_{49}NO_{12}$.—Melts at 259.1° and is optically inactive.

Protoveratrine, $C_{32}H_{51}NO_{11}$.—Melts with charring at 245°-250°.

Protoveratridine, $C_{26}H_{45}NO_8$. Melts at 265° ; non-poisonous.

8. Additional Alkaloids.—*Aspidospermine*, $C_{22}H_{30}N_2O$, and *Quebrachine*, $C_{21}H_{26}N_2O_3$, are found, along with other alkaloids, in the bark of *Aspidosperma Quebracho.*

Berberine, $C_{20}H_{17}NO_4.5\frac{1}{2}H_2O$, is found in the root of *Berberis vulgaris* and *Hydrastis canadensis.* It forms yellow needles, melting at 120°. When fused with caustic potash it yields quinoline. Associated with it in *Hydrastis canadensis* is the alkaloid *Hydrastine*, $C_{21}H_{21}NO_6$, which forms colorless prisms, melting at 132°, and *Canadine*, $C_{21}H_{21}NO_4$, which forms white, shining crystals, melting at 134°.

Physostigmine, $C_{15}H_{21}N_3O_2$, is found in *Physostigma venenosum* (Calabar bean). It forms colorless or pinkish crystals, only slightly soluble in water, soluble in alcohol and ether. Two of its salts are now official, **Physostigminæ Salicylas**, U. S. P., and **Physostigminæ Sulphas**, U. S. P.

Pilocarpine, $C_{11}H_{16}N_2O_2$, is an alkaloid found in the several varieties of *Pilocarpus.* It is a crystalline alkaloid first found in Jaborandi leaves, but since made synthetically by Hardy and Calmels from β-pyridine-α-lactic acid by first forming pilocarpidine, $C_{10}H_{14}N_2O_2$, and then converting this by the action of methyl iodide into pilocarpine. Two of its salts are official, **Pilocarpinæ Hydrochloras**, U. S. P., and **Pilocarpinæ Nitras**, Br. P.

Piperine, $C_{17}H_{14}NO_3$ (**Piperinum**, U. S. P.), is obtained from the black and white pepper, in which it is found to the amount of from 7 to 9 per cent. It is a weak alkaloidal base, forming pale yellowish crystals, melting at 130°. When heated with alcoholic potash it is decomposed into *Piperidine*, $C_5H_{11}N$, and *Piperic acid*, $C_{12}H_{10}O_4$. The first of these compounds has already been noticed as hexahydropyridine (see p. 751), and the second is related to the oxyacids of the benzene series, and yields piperonal (see p. 718) by its oxidation.

Piperine can be made synthetically by the action of piperidine on the acid chloride, $C_{12}H_9O_3Cl$.

ANIMAL ALKALOIDS, PTOMAINES, AND LEUCOMAINES.

While it was pointed out as far back as 1820 that symptoms of poisoning would be developed by introducing into an animal products of decomposing and putrefying organic matter, it has only been since 1870, when the Italian Selmi published his studies on cadaveric poisons, that the subject has been fully appreciated.

He gave the name of "ptomaïnes" to these poisonous products of putrefaction. In 1884, Poehl, of St. Petersburg, in the report of a commission appointed to investigate the subject, stated the following conclusions :

1. Putrefaction, fermentation, and other as yet indefinite alterations of albuminous substances are accompanied by the generation of alkaloid-like bodies,—ptomaïnes.

2. These ptomaïnes may be fixed or volatile, fluid or solid, amorphous or crystalline. They show an alkaline reaction, and form salts with the acids like the alkaloids.

3. Some ptomaïnes are tasteless or odorless; others possess an intense bitter taste or aromatic, sweetish odor. Others, again, evolve a cadaveric odor, or resemble conine or nicotine. They are optically inactive bodies. Their color reactions are as various as those of the vegetal alkaloids, and often simulate them.

Gautier, in 1881, announced the presence of toxic alkaloids in the excretions of animals, and gave to them the name of "leucomaïnes." His explanation of their occurrence is as follows: "While four-fifths of the products of animal combustion are aërobic formations, the remaining part of the combustion of the animal economy takes place at the expense of the tissues and is anaërobic, oxygen taking no part in it. In a normal condition of the body a very small proportion of muscular leucomaïnes is found in urine. But if the air that reaches the blood be diminished in quantity, or if the proportion of hæmoglobin be diminished, as in chlorosis or anæmia, or if substances be introduced into the blood which prevent hæmatosis, substances of the character of leucomaïnes or ptomaïnes accumulate in the blood."

Nitrogenous substances, not alkaloids, which are still poisonous are also formed. These have been named "toxalbumens" or "albumoses."

Among the non-oxygenated liquid ptomaïnes may be enumerated :

Dimethylamine, *Triethylamine*, *Propylamine* (see p. 629), These are monamines.

In the class of diamines (see p. 630) we have: *Putrescine*, $C_4H_{12}N_2$ (tetramethylene-diamine), *Cadaverine*, $C_5H_{14}N_2$ (pentamethylene-diamine). These have both been described on p. 630. Isomeric with the last is *Neuridine*, a non-poisonous ptomaïne from the decomposition of flesh.

Hydrocollidine, $C_{11}H_{18}N$, is a very poisonous ptomaïne found by Gautier in decomposing horse-flesh. *Collidine*, $C_8H_{11}N$ (tri-

CHAPTER IX.

THE TERPENES AND THEIR DERIVATIVES.

I. THE TERPENES.

THE terpenes are hydrocarbons of the formula $(C_5H_8)_x$. Both they and the camphors, which are oxygenated derivatives, show a close relationship to the aromatic hydrocarbons, as common camphor, $C_{10}H_{16}O$, by the action of certain dehydrating agents yields cymene, $C_{10}H_{14}$, and terpenes of the formula $C_{10}H_{16}$ when heated with iodine are oxidized and yield the same hydrocarbon $C_{10}H_{14}$. We may therefore consider the terpenes as hydrogen addition compounds of benzene hydrocarbons.*

Characteristic Reactions.—Besides the production of cymene by oxidation, we have other distinctive reactions. The terpenes of the formula $C_{10}H_{16}$ may add on one or two molecules of a haloid acid (HCl, HBr, HI) or the corresponding amount of bromine, showing that they are unsaturated and that their molecules contain either one or two double linkings of carbon atoms. Many terpenes also form characteristic compounds with nitrous acid, called *nitrosites*, such as $C_{10}H_{16}N_2O_3$. These are crystalline compounds, and may be availed of for the separation of many terpenes. Most terpenes also combine with *nitrosyl-chloride*, NOCl, forming *nitrosochloride-terpenes*. These also are crystalline compounds, which combine with organic bases like benzylamine and piperidine to form *nitrolamines*.

Some terpenes form with water crystalline hydrates, as terpin-hydrate, $C_{10}H_{16}(H_2O)_2 + H_2O$. This combination takes place especially in the presence of dilute nitric acid and alcohol. The terpenes frequently polymerize by heating under pressure or by shaking with concentrated sulphuric acid.

Many terpenes are optically active. Frequently a lævo rotatory and a dextro-rotatory modification of the same terpene may be obtained, which, when mixed, yield an optically inactive variety.

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* A full discussion of the theoretical views held as to the structural formulas of the terpenes and their derivatives by Professor Ed. Kremers, in which Baeyer's proposed system of nomenclature for these compounds is given, will be found in "Proceedings of the American Pharmaceutical Association, 1894."

sylvestrene and dipentene it makes up the Russian and Swedish turpentine oils.

Oil of Turpentine (**Oleum Terebinthinæ, U. S. P.**) is distilled from the oleo-resin (crude or virgin turpentine) obtained from *Pinus palustris* (*australis*). The European turpentine is chiefly obtained from *Pinus sylvestris* and *Pinus maritima;* Venice turpentine from *Larix Europæa;* the Strassburg turpentine from *Pinus picea;* Canadian turpentine or Canada balsam from *Abies balsamea.*

The oleo-resin is distilled with steam, whereby the terpenes distil over, leaving as a residue *colophony* resin, which accompanied the essential oil in the original exudation.

The crude oil may be further rectified according to the Pharmacopœial process by distilling with lime water. It then forms a "thin, colorless liquid, of characteristic odor and taste, both of which become stronger and less pleasant by age and exposure to the air." Sp. gr. 0.855 to 0.870. It boils when rectified at 160°. It is almost insoluble in water, easily soluble in alcohol and ether. It dissolves resin, caoutchouc, sulphur, phosphorus, etc. Turpentine oil, like many other mixtures of terpenes, readily absorbs oxygen, and hydrogen dioxide is formed. The oil is then capable of turning guaiacum tincture blue, liberating iodine from potassium iodide, and producing other reactions characteristic of ozone and hydrogen dioxide. Strong nitric acid inflames the oil, but oxidized by dilute nitric acid it yields acids of both the methane series, like butyric, propionic, acetic, and oxalic, and the benzene series like terephthalic and para-toluic. Treated with bromine or iodine it yields cymene.

The American and Russian turpentine oils are right-rotatory, the French, German, and Venetian oils are left-rotatory. These differences are due to the existence of the right and left rotatory varieties of pinene. Inactive pinene may be obtained by heating the pinene nitrosochloride with aniline, whereby NOCl is split off.

Pinene unites with one molecule of HCl to form *Pinene hydrochloride*, $C_{10}H_{17}Cl$, a white solid, melting at 125°, and resembling camphor in appearance and odor, whence the name "artificial camphor." It is insoluble in water, soluble in alcohol. When heated with soaps or weak alkali it splits off hydrochloric acid again and leaves camphene, $C_{10}H_{16}$.

When turpentine oil stands in contact with water, especially in the presence of nitric acid and alcohol, it unites with three molecules of water to form a hydrate, $C_{10}H_{18}(OH)_2 + H_2O$, known as *Terpin Hydrate* (**Terpini Hydras,** U. S. P.). This is in colorless rhombic prisms of slightly aromatic and somewhat bitter taste, melting at 116°–117°. The anhydrous *terpin*, $C_{10}H_{18}(OH)_2$, obtained in this fusion, or by drying over sulphuric acid, has somewhat of a glycol (or diatomic alcohol) character. When distilled with dilute sulphuric acid it loses a molecule of water and yields *terpineol*, $C_{10}H_{17}(OH)$, an oil of hyacinthine odor which is used in medicine. Still further heating changes it into a mixture of dipentene, terpinene, and terpinolene, all terpenes of the formula $C_{10}H_{16}$.

When sulphuric acid is allowed to stand in contact with oil of turpentine, and the mixture, after a day's standing, is heated to boiling, the oil is changed into an optically inactive mixture of terpenes known as *Terebene* (**Terebenum,** U. S. P.). The Pharmacopœia states that terebene "consists chiefly of pinene, and contains not more than very small proportions of terpinene and dipentene," while Dr. F. B. Power, as the result of a recent research, states that it consists chiefly of the hydrocarbons dipentene and terpinene, with some cymene and camphene. The Pharmacopœia gives the boiling point as 156°–160°, while Dr. Power makes it 170°–185°.

Camphene may be obtained, as already mentioned, by the decomposition of pinene hydrochloride by soap, or with alcoholic potash, also from bornyl chloride, $C_{10}H_{17}Cl$. It exists as dextro- and lævo-camphene. Camphene forms a solid crystalline mass, fusing at 49°, and smelling of turpentine and camphor. It is more stable than pinene, but it is oxidized by chromic acid mixture to common camphor. The addition-compound formed with one molecule of HCl is unstable.

Limonene.—The dextro-limonene, known also as *hesperidene*, *citrene*, or *carvene*, is almost the exclusive constituent of oil of orange-peel, and the chief constituent of oils of dill, caraway, and erigeron. Mixed with pinene it forms lemon oil. It boils at 175°, and forms a tetrabromide, $C_{10}H_{16}Br_4$, fusing at 104°, and dextro-rotatory in character. It is readily changed into inactive limonene or dipentene.

Lævo-limonene is found, according to some authorities, along with lævo-pinene in oil of Norway spruce, although Drs. Bertram and Walbaum. of Schimmel & Co.'s laboratory, state that the limonene of this oil is inactive. The dextro- and lævo-limonene tetrabromides, both fusing at 104°, unite to form a dipentene tetrabromide fusing at 125°.

Dipentene (*Cinene* or *inactive Limonene*) is found in cajuput and camphor oils along with cineol. It is formed from pinene, camphene, limonene, etc., by heating these for several hours to 250°–270°. It is also formed from pinene under the influence of dilute alcoholic sulphuric acid, from terpin hydrate by the splitting off of water, from isoprene by polymerization, from caoutchouc by distillation along with isoprene, and in other ways. It forms a pleasant-smelling liquid with an odor of lemons, boiling at 175°–176°. It readily forms a dihydrochloride and a tetrabromide, both of which have been given in the table (see p. 779). It is more stable than pinene. Its nitrosochloride, by the splitting off of hydrochloric acid, yields a nitrosodipentene, known also as inactive *carvoxine*, fusing at 93°.

Sylvestrene is the dextro-rotatory constituent of Swedish and Russian turpentine oils. It boils at 175°, and is one of the most stable of the terpenes. With acetic anhydride and concentrated sulphuric acid it yields a fine blue color. Its dihydrochloride fuses at 72°, and is dextro-rotatory.

Terpinolene is very similar to dipentene.

Terpinene.—This and the preceding terpene both result from the isomerization of pinene and limonene (see Terpin Hydrate, p. 781). Terpinene forms a nitrosite.

Phellandrene is found in a dextro-rotatory variety in oil of water-fennel, and in a lævo-rotatory variety in oil of *Eucalyptus amygdalina*. It unites readily with nitrous acid to form a solid nitrosite. It is one of the least stable of the terpenes, and readily changes into dipentene, and when treated with alcoholic hydrochloric acid into terpinene.

Sesquiterpenes, $C_{15}H_{24}$.—Hydrocarbons of this formula occur in oils of cubebs and patchouly, and may also be obtained synthetically by the heating of the unsaturated hydrocarbon valerylene, C_5H_8, to 250°–260° under pressure, or by the action of concentrated sulphuric acid upon it. They are all liquid.

Diterpenes, $C_{20}H_{32}$.—Such hydrocarbons are found in copaiba balsam, and are formed by the superheating of turpentine oil. *Colophene*, the residue formed in the manufacture of terebene, is also of this class. It is a thick oil, boiling at 318°.

Polyterpenes, $(C_{10}H_{16})_x$.—These may be obtained by the polymerization of oil of turpentine under the influence of antimony trichloride. They boil at over 250°, and are lævo-rotatory. The terpenes of caoutchouc and gutta-percha probably belong in this class also.

flame. Its sp. gr. is 0.985. The natural camphor is dextro-rotatory; the artificial camphor is dextro- or lævo-rotatory according to the character of the camphene from which it is prepared. Under the influence of phosphoric oxide it splits off water, yielding cymene. Heated with iodine it yields carvacrol (see p. 708). As camphor combines with both hydroxylamine and phenylhydrazine, it is of ketone character. This is also shown by its relation to the secondary alcohol borneol.

By the action of bromine in proper proportion upon camphor we obtain a bromine substitution compound known as *Monobromated Camphor*, $C_{10}H_{15}BrO$ (**Camphora Monobromata** U. S. P.). This forms "colorless, prismatic needles, with a mild camphoraceous odor and taste, permanent in the air, unaffected by light, and neutral to litmus paper." It melts at 76° and sublimes at a slightly higher temperature.

Isomeric with camphor are ***pinol***, obtained artificially from pinene; ***absinthol***, contained in oil of wormseed; ***fenchol*** (or *fenchone*), contained in oil of fennel.

Borneol, $C_{10}H_{18}O$.—Borneol (or Borneo camphor) has been found in the wood of *Dryobalanops aromatica*, and is contained also chiefly in the form of esters in the oils of rosemary, Spanish thyme, valerian, citronella, and the different pine oils. Borneol forms crystals melting at 203°–204° and boiling at 212°, and possessing an odor recalling patchouly and ambergris. When common camphor is reduced by metallic sodium, the product, commercially known as borneol, is a mixture of true borneol and *iso-borneol*. This latter melts at 212°, and has more the odor of tansy and sage. Among the esters of borneol may be mentioned *bornyl acetate*, found in the pine-needle oils, and *bornyl formate* and *bornyl valerianate*, found in oil of valerian.

Isomeric with borneol are *cineol* (*eucalyptol*), found in oils of cajuput, camphor, lavender, rosemary, wormseed, eucalyptus, etc., and *terpineol*, found in oils of cajuput and Japanese valerian, and made synthetically, along with cineol, from terpin by the splitting off of water. By the action of sulphuric acid terpineol is changed into cineol.

Isomeric with borneol are also *linalool* and *geraniol*, two monatomic unsaturated alcohols, which either by themselves or through their esters play a very important part in the composition of many of the essential oils.

Linalool, $C_{10}H_{17}OH$, is the essential and fragrant constituent of oil of linaloe, and is found either free or in the form of esters

III. THE ESSENTIAL OILS.

By the distillation of the blossoms, flowers, and fruit of many plants with steam are obtained a class of products known as the *essential* or *volatile oils*. They are distinguished both by physical and chemical differences from the *fixed* or *fatty oils*. These latter (see p. 621) are largely mixtures of the glycerin esters of the fatty acids, often containing, in addition, the fat acids in the free state. While the essential oils show some variations in their chemical composition, they are in the main mixtures of terpenes and camphors, although esters of these latter occur, and in a few instances we have aldehydes and ketones.

The fixed oils belong in the aliphatic or methane series of derivatives, while the essential oils all show cyclic or aromati derivatives among their constituents. The essential oils als show a tendency to absorb oxygen on prolonged exposure to th air and to form resinous products.

Physically the essential oils are characterized by their entir volatility without residue, while the fatty oils are decomposed b heat before volatilization can be completed, and yield acrolein an similar products of decomposition.

The specific gravity of the essential oils is generally less tha that of water, and hence they separate on its surface in th product of the steam distillation. They are only very slight soluble in water, but easily soluble in strong alcohol, chlorofor ether, benzene, and fatty oils. They leave a transient spot on upon paper, while the fixed oils leave a permanent "grease-spot

The extraction of the essential oils from the plants containi them may be effected:

1. By *distillation*, usually with steam, although in rare ca without. A Florentine receiver is frequently employed to coll the distillate, and by this means the separation of the light, oil layer from the accompanying water is effected.

2. By *expression*. This is followed in cases where the oil *is* abundant and readily separable, as with oil of lemon, orange peel, etc.

3. By *extraction with solvents*. This solvent may be a liquid fat, as in the case of maceration, a solid fat, as in the case of *enfleurage*, or a volatile solvent, as in the extraction of fine or costly perfumes.

The official essential oils and their proximate chemical composition are as follows:

known as *carvene*) and dextro-rotatory *carvol*. This body is chemically a ketone of the composition $C_{10}H_{14}O$, and is a liquid boiling at 224°.

Oleum Caryophylli, U. S. P. (Oil of Cloves), is "a pale yellow, thin liquid, becoming darker and thicker by age and exposure to the air, with a strong aromatic odor of cloves, and a pungent and spicy taste." The oil contains *eugenol* (oxy-methoxy-allyl-benzene, $C_6H_3\left\{\begin{matrix}C_3H_5\\OCH_3\\OH\end{matrix}\right)$) to the amount of 80 to 90 per cent., and a sesquiterpene termed *caryophyllene*, which boils at 255°. Eugenol, the chief constituent, forms a colorless liquid with the odor and taste of cloves. It has a sp. gr. 1.072, and boils at 253°–254°. It is also found in other essential oils, such as pimenta, bay, Ceylon cinnamon, sassafras, and camphor.

Oleum Chenopodii, U. S. P. (Oil of Chenopodium, or American Wormseed), is a yellowish liquid, with a penetrating odor, and pungent, bitterish taste. It is stated to contain a terpene, $C_{10}H_{16}$, and a body of the formula $C_{10}H_{16}O$.

Oleum Cinnamomi, U. S. P. (Oil of Cinnamon or Oil of Cassia).—"A yellowish or brownish liquid, becoming darker and thicker by age and exposure to the air, with the characteristic odor of cinnamon, and a sweetish, spicy, and burning taste." It consists chiefly of *cinnamic aldehyde*, $C_8H_7.COH$, with some *cinnamyl acetate*, $C_9H_9.C_2H_3O_2$. The amount of cinnamic aldehyde should not be less than 75 per cent.

Oleum Copaibæ, U. S. P. (Oil of Copaiba), is distilled from the so-called Balsam of Copaiba. "It forms a pale yellowish liquid, with the characteristic odor of copaiba, and an aromatic, bitterish, and pungent taste." The oil consists chiefly of *caryophyllene*, $C_{15}H_{24}$.

Oleum Coriandri, U. S. P. (Oil of Coriander), is distilled from the fruit of *Coriandrum sativum*. The oil contains linalool (formerly known as *coriandrol*) and pinene.

Oleum Cubebæ, U. S. P. (Oil of Cubeb), is "a colorless, pale greenish or yellowish liquid, having the characteristic odor of cubeb, and a warm, camphoraceous, aromatic taste." The oil consists chiefly of *cadinene*, $C_{15}H_{24}$, with some dipentene, and when old, or distilled from old fruit, contains *cubeb camphor*, $C_{15}H_{24}.H_2O$.

Oleum Erigerontis, U. S. P. (Oil of Erigeron or Fleabane), is "a pale yellow, limpid liquid, becoming darker and thicker by age and exposure to the air, having a peculiar, aromatic, persistent odor, and an aromatic, slightly pungent taste." It consists chiefly of dextro-rotatory limonene, together with a substance readily decomposing or polymerizing by heat.

Oleum Eucalypti, U. S. P. (Oil of Eucalyptus), is "a colorless or slightly yellowish liquid, having a characteristic, aromatic, somewhat camphoraceous odor, and a pungent, spicy, and cooling taste." The oil from the *E. globulus* contains cineol (eucalyptol), dextro-rotatory pinene, and small amounts of valeric, butyric, and caproic aldehydes. The oil from *E. oleosa* (which is also included as an official source of eucalyptus oil) contains cineol and cuminol. Both of these eucalyptus oils have strongly antiseptic properties due to the cineol (eucalyptol) contained in them.

Oleum Fœniculi, U. S. P. (Oil of Fennel), is distilled from the fruit of *Fœniculum capillaceum.* It contains pinene, phellandrene, dipentene, *fenchone,* $C_{10}H_{16}O$, and anethol, $C_{10}H_{12}O$, the latter usually in amounts of about 60 per cent. The higher the temperature at which the crystals of anethol separate the better the quality of the oil. Oil of fennel from different sources may differ, and one or more of the above-named constituents may be absent.

Oleum Gaultheriæ, U. S. P. (Oil of Gaultheria or Wintergreen), is distilled from the leaves of *Gaultheria procumbens.* The oil is substantially identical with oil of sweet birch (see p. 787), and consists chiefly of methyl salicylate with a fraction of 1 per cent. of a hydrocarbon, $C_{15}H_{24}$.

Oleum Hedeomæ, U. S. P. (Oil of Hedeoma or American Pennyroyal), distilled from the leaves and tops of *Hedeoma pulegioides.* The oil contains *pulegone,* $C_{10}H_{16}O$, together with two ketones of the formula $C_{10}H_{18}O$ (one being apparently menthone), and formic, acetic, and isoheptoic acids.

Oleum Juniperi, U. S. P. (Oil of Juniper).—It may vary in optical properties, and show either dextro-rotatory, lævo-rotatory, or inactive character. It consists chiefly of pinene, with some cadinene, $C_{15}H_{24}$, and an undetermined substance, probably an ester, to which the peculiar juniper-like odor and taste are due.

Oleum Lavandulæ Florum (Oil of Lavender Flowers).—The oil contains linalool, linaloyl acetate, geraniol, and a very small amount of cineol.

Oleum Limonis, U. S. P. (Oil of Lemon), is obtained by expression from fresh lemon peel, the rind of the recent fruit of *Citrus Limonum.* It contains a small amount of pinene with dextro-rotatory limonene, about 7 to 8 per cent. of *citral* (see p. 785), and a small amount of citronellal.

Oleum Menthæ Piperitæ, U. S. P. (Oil of Peppermint).—"A colorless, yellowish or greenish-yellow liquid, becoming darker and thicker by age and exposure to the air, having the characteristic strong odor of peppermint, and a strongly aromatic, pungent taste, followed by a sensation of cold when air is drawn into the mouth."

The results of an investigation conducted in the laboratory of Fritsche Bros. at Garfield, N. J., show that the composition of American peppermint oil is quite complex, the following constituents having been noted:

Acetaldehyde.
Acetic acid.
Isovaleraldehyde.
Isovalerianic acid.
A liquid acid, $C_8H_{12}O_2$.
Pinene.
Phellandrene.
A lactone, $C_{10}H_{16}O_2$.
Limonene.
Cineol.
Menthone.
Menthol.
Menthyl acetate.
Menthyl isovalerianate.
Cadinene.

Oleum Menthæ Viridis, U. S. P. (Oil of Spearmint), is distilled from the fresh herb of *Mentha viridis.* The oil co[illegible]vo-rotatory carvol and lævo-rotatory limonene, with possibly [illegible].

Oleum Myrciæ, U. S. P. (Oil of Myrcia or Oil of Bay), is
or brownish-yellow liquid, having an aromatic, somewhat clo
and a pungent, spicy taste. The oil, according to Mittmann,
penes, a considerable amount of eugenol, a little of the me
eugenol, $C_6H_3(OCH_3)_2.C_3H_5$, and apparently a diterpene,

Oleum Myristicæ, U. S. P. (Oil of Nutmeg), is distilled f
the seed of *Myristica fragrans* deprived of its testa. It co
of pinene, with probably some dipentene, also *myristicol,* C
myristicin, $C_{12}H_{14}O_2$.

Oleum Pimentæ, U. S. P. (Oil of Pimenta or Oil of All
distilled from pimenta, the nearly ripe fruit of *Pimenta offi*
oil contains eugenol and a sesquiterpene, $C_{15}H_{24}$.

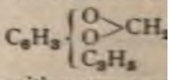
Oleum Rosæ, U. S. P. (Oil of Rose), is distilled from the
of *Rosa damascena.* Oil of rose when slowly cooled to bet
21° becomes a transparent solid, interspersed with nume
scale-like crystals. The liquid fragrant portion of the oil co
most part of an alcoholic body of the composition $C_{10}H$
first was called *rhodinol,* but is now recognized to be si
geraniol (see p. 785). The solid crystallizable portion,
"stearopten," of the oil is odorless when pure, and consists
of several hydrocarbons, one of which melts at 35.5° to 36.5
composition $C_{20}H_{42}$.

Oleum Rosmarini, U. S. P. (Oil of Rosemary), is "a colo
yellow, limpid liquid, having the characteristic, pungent
mary, and a warm, somewhat camphoraceous taste." The
pinene, cineol, borneol, and camphor.

Oleum Sabinæ, U. S. P. (Oil of Savine), is distilled from
Juniperus sabinæ. The oil contains pinene and cadinene, C

Oleum Santali, U. S. P. (Oil of Santal or Sandal-wood
from the wood of *Santalum album.* The East Indian or
santal contains, according to Chapoteaut, a body called *santa*
boiling at 300°, together with a smaller amount of an alc
santalol, $C_{15}H_{26}O$, which boils at 310°, and is converted b
oxide into *santalene,* $C_{15}H_{24}$, boiling at 260°.

Oleum Sassafras, U. S. P. (Oil of Sassafras), is distilled f
of the root of *Sassafras variifolium.* The oil consists chi
(methylene ester of allyl-dioxybenzene),



$C_6H_3\left\{\begin{array}{l}\left.\begin{array}{l}O\\O\end{array}\right>CH\\C_3H_5\end{array}\right.$

liquid, boiling at from 232° to 233°, together with a very sma
eugenol and a dextro-rotatory hydrocarbon termed *safr*
which is probably identical with pinene.

Oleum Sinapis Volatile, U. S. P. (Volatile Oil of Mustard
from black mustard, the seed of *Brassica nigra,* by macerati
and subsequent distillation. It consists chiefly of allyl isosu
$CS{=}N(C_3H_5)$, with traces of carbon disulphide. These p
from the decomposition of the glucoside *sinigrin* (see chap
sides) under the influence of a naturally occurring ferment n

Mustard oil is also made artificially by treating allyl iodi latter of which is used extensively in the manufacture of printer's ink.

Dammar (from *Dammara orientalis* and *D. australis*).—The East Indian dammar is an exudation; the New Zealand dammar, known also as "Kauri resin," is found fossil as well as of present formation. The resin is harder than colophony; only partially soluble in alcohol, more soluble in ether, chloroform, and benzene. About 1 per cent. of resin acid only is present. The chief use is for varnishes.

Copal, which is found fossil in Zanzibar and on the West Coast of Africa, is the hardest of these resins, and is especially valuable for the manufacture of varnishes.

Amber (a fossil resin from *Picea succinifera*) is found along the shores of the Baltic and other localities. It melts at 287.5, giving off succinic acid, and at a higher heat, volatile acids and empyreumatic oil of amber.

Lac Resin is an exudation resulting from the puncture of trees by the female insect *Coccus lacca*. The "stick-lac" forms thin branches covered with a brown-red resin; "seed-lac" is in somewhat rounded fragments detached from the twigs; "shellac" is the purified resin solidified in thin layers of amber to brown color.

Guaiac Resin is an exudation from the bark of the *Guaiacum officinale*, or melted out of the heart wood by heat. Its alcoholic solution is colored blue on the addition of ferric chloride, chlorine, chromic acid, and other oxidizing agents. The resin fused with caustic potash yields protocatechuic acid. Destructively distilled, it yields guaiacol, creosol (see p. 710), and other products.

Dragon's Blood is a red resin obtained as an exudation from the fruit of *Calamus draco*, growing in Sumatra, Borneo, and adjacent islands. It may contain benzoic and cinnamic acids in small amount. It is used in colored varnishes and various preparations.

Mastic (Mastiche) is obtained as an exudation from incisions in the bark of *Pistacia lentiscus*, and is collected in the island of Scio. It contains from 1 to 2 per cent. of volatile oil, together with two resins. It is used for cements and varnishes.

Sandarac is also obtained as an exudation. Is used chiefly for varnishes of the alcohol or spirit class.

Benzoin (from *Styrax Benzoïn*) is obtained from Sumatra, Java, and Siam. It has an aromatic, acrid taste and an agreeable balsamic odor, and contains from 12 to 20 or 24 per cent. of benzoic acid, cinnamic acid, and several resins, which, fused with caustic potash, yield para-oxybenzoic acid, protocatechuic acid, and pyrocatechin.

Xanthorrhœa Resin (Acaroid or Botany Bay Resin) is obtained in Australia from *Xanthorrhœa hastilis.* It contains benzoic acid, some cinnamic acid, and resins. Is used in the preparation of varnishes.

2. **Oleo-resins and Balsams.**—The oleo-resins are mixtures of resins and volatile oils. Those liquid or soft products which contain benzoic and cinnamic acids, in addition to the resin, are generally given the special designation of balsams.

Turpentines (*Terebinthinæ*).—Under this heading may be included the oleo-resins known as common or American turpentine (from *Pinus australis* and *P. tæda*), French or Bordeaux turpentine (from *P. maritima*), Canada balsam (from *Abies balsamea*), Strassburg turpentine (from *Abies pectinata*), Venice turpentine (from *Larix Europæa*), and Russian turpentine (from *Pinus sylvestris* and *P. Ledebourii*). The composition of these several natural mixtures has already been stated under **Oleum Terebinthinæ** (see p. 780).

Burgundy Pitch (**Pix Burgundica,** U. S. P.) and *Canada Pitch* (Hemlock Pitch) are both natural oleo-resins, the former exuding from incisions in the *Abies excelsa*, and the latter from *Tsuga Canadensis.*

Wood Tar (**Pix Liquida,** U. S. P.), on the other hand, is a product of the destructive distillation of the wood of the different species of *Pinus.* It is a very complex mixture, containing pyroligneous acid, acetone, and methyl alcohol, toluene and several of its homologues, naphthalene, pyrene, chrysene, paraffine, phenols, and their esters.

Juniper Tar (see Oil of Cade, p. 787) and *Birch Tar* are similar products of destructive distillation.

Copaiba Balsam (**Copaiba,** U. S. P.) is the oleo-resin of *Copaiba Langsdorfii*, and contains, besides the sesquiterpene *caryophyllene*, resins, of which one, *copaivic acid*, $C_{20}H_{30}O_2$, is crystalline.

Elemi is an oleo-resin exuding from incisions in *Canarium commune*, in the Philippine Islands. It contains, besides volatile oil, a mixture of resins (breïn, amyrin, bryoïden, breïdin, and elemic acid).

Gurjun Balsam (Wood Oil) is a liquid exudation from the species of *Dipterocarpus*, and contains volatile oil, said to be identical with oil of copaiba, and resin.

Peru Balsam (**Balsamum Peruvianum,** U. S. P.) is of a syrupy consistence and reddish-brown color, with a balsamic and smoky odor. The oily liquid which separates on agitation with caustic potash, called cinnamein, is made up of benzyl alcohol, benzyl benzoate, and benzyl cinnamate. The resin, which is admixed with the oil, yields by dry distillation benzoic and cinnamic acids, styrene, and toluene, together with styracine (cinnamyl cinnamate).

Tolu Balsam (**Balsamum Tolutanum, U. S. P.**) is a balsam obtained from *Toluifera Balsamum*, a tree growing in Venezuela and New Grenada.

The balsam is at first semi-solid, but becomes harder by age. It contains benzyl benzoate and cinnamate, free benzoic and cinnamic acids, *tolene*, $C_{10}H_{16}$, and two resins, which make up over 80 per cent. of the balsam.

Liquidambar (Sweet Gum) is an exudation from *Liquidambar styraciflua*. It is a thick brownish-yellow liquid or solid resin. It contains a mixture of cinnamic esters, the hydrocarbon styrol (or cinnamene), C_8H_8, and two resins known as α-storesin and β-storesin.

Storax (**Styrax, U. S. P.**) is a balsam obtained from *Liquidambar orientalis*. The principal constituent is ***storesin***, $C_{36}H_{55}(OH)_3$, and its cinnamic ester. Several other esters of cinnamic acid, a little vanillin, and styrol or cinnamene are the other constituents.

3. **Gum-resins.**—These are milky exudations from plants, and contain gum which is wholly or partly soluble in water and resin soluble in alcohol. Many gum-resins also contain essential oil. Of this class are *Asafetida* (**Asafœtida, U. S. P.**). It is a gum-resin obtained from the root of *Ferula fœtida*. It contains from 3 to 9 per cent. of volatile oil (containing sulphur), 20 to 30 per cent. of gum, and 50 to 70 per cent. of resin. This latter contains a little ferulaic acid (see p. 729), on dry distillation yields umbelliferon, and fused with caustic potash gives resorcin and protocatechuic acid.

Galbanum is a gum-resin brought from Persia. It contains from 6 to 9 per cent. of volatile oil, gum, and from 60 to 66 per cent. of resin. This latter also yields umbelliferon, $C_9H_6O_3$, on distillation, and resorcin on fusion with caustic potash.

Sagapenum is a very closely-related gum-resin.

Ammoniac (**Ammoniacum, U. S. P.**).—A gum-resin obtained from *Dorema ammoniacum*. It contains volatile oil (free from sulphur), gum, and resin. It does not yield umbelliferon on distillation, but does yield resorcin and protocatechuic acid on fusion with caustic potash.

Olibanum (or Frankincense) is a gum-resin exuding from the several species of *Boswellia* in Eastern Africa and Southern Arabia. It contains from 4 to 7 per cent. of essential oil, from 56 to 72 per cent. of resin, and about 30 per cent. of gum. When burned it develops a strongly aromatic odor.

Myrrh (**Myrrha**, U. S. P.) is a gum-resin exuding from the *Commiphora Myrrha* in Eastern Africa and Southwestern Arabia. It contains from 2 to 4 per cent. of volatile oil, from 25 to 40 per cent. of resin, and from 40 to 60 per cent. of gum. Fused with caustic potash the resin yields pyrocatechin and protocatechuic acid. It is used extensively in the form of tincture and powders.

Bdellium is a gum-resin very similar in character to myrrh.

Gamboge (**Cambogia**, U. S. P.) is a gum-resin exuding as a milky juice from incisions in *Garcinia Hanburii*, and is collected in bamboo joints, and comes into commerce in cylindrical pieces. It forms a yellow emulsion with water. It contains 16 to 26 per cent. of gum, 66 to 80 per cent. of resin or *cambogic acid*, and about 4 per cent. of wax.

Euphorbium is an exudation from incisions in the stem of the *Euphorbia resinifera* from Morocco. It contains 18 per cent. of gum, 38 per cent. of resin, some starch, malates, and ash.

Scammony (**Scammonium**, U. S. P.) is a milky juice collected in Western Asia from the *Convolvulus Scammonia.* It forms a greenish emulsion with water. It contains from 75 to 90 per cent. of resin, known as *scammonin*, $C_{34}H_{56}O_{16}$, identical with the *orizabin* of *Ipomea orizabensis*, and converted by alkalies into scammonic acid, which is soluble in water. The rest of the drug is gum, soluble in water.

CHAPTER X.

GLUCOSIDES—BITTER AND NEUTRAL PRINCIPLES.

I. GLUCOSIDES.

UNDER this name have been grouped a number of compounds, occurring mainly in the vegetable kingdom, that under the influence of dilute acids or ferments are split up into component parts, of which glucose or a related carbohydrate always is one. The glucosides appear to be, not esters, but ethers, which, under the treatment above referred to, take up the elements of water, and then yield the glucose and other products.

While sharing this method of decomposition in common they show in other respects a wide divergence. Thus, solanin is a nitrogenous base, and is thus at once an alkaloid and a glucoside, while other glucosides, like myronic acid, are of well-defined acid character. The most of the glucosides, however, are neutral bodies, although they frequently combine with metallic oxides, such as lead and mercuric oxides. They are usually soluble in water and in alcohol, often insoluble in ether, and generally crystallizable. On heating with concentrated sulphuric acid and the bile acids, the glucosides give, like the sugars, the Pettenkofer bile reaction,—viz., a deep-red color. Alkaline copper solution is reduced by most, but not all, of the glucosides. Ammoniacal silver solution is reduced by glucosides, as by cane-sugar and mannite, only after the addition of caustic alkali. Many glucosides are optically active, most of them showing a lævo-rotatory character. This rotatory power does not, however, correspond in any way to that of the sugar, which is obtained by the decomposition of the glucoside.

Glucosides, as a rule, are not decomposed by pure water, even on boiling or heating under pressure, but dilute acids readily effect the decomposition, sulphuric and hydrochloric being chiefly used. Alkalies may also effect the decomposition, although baryta water is better adapted, as the stronger alkali generally acts upon the sugar liberated, decomposing or altering it. The splitting up of the glucosides is, however, often best effected by the action of ferments, which may act at the ordinary or only slightly elevated temperature. Among such ferments may be mentioned *emulsin*, an albuminoid found in the almond; *myrosin*, found in mustard-seed; and the ferment contained in the saliva.

For the extraction of glucosides from the plant it frequently suffices to extract with water or alcohol, and to crystallize the glucoside from the concentrated extracts after decolorizing with animal charcoal; or, after defecating the decoction from the plant with neutral acetate of lead, which does not affect the glucoside as a rule, the addition of basic lead acetate will precipitate it in the form of a weak combination readily decomposed by hydrogen sulphide. Tanret has proposed still another procedure. After leaving the finely-pulverized plant material in contact with milk of lime for 24 hours, he extracts with distilled water in a displacement apparatus, and precipitates these extraction liquors with a concentrated solution of sodium chloride; the precipitate is dried, preferably in vacuo, and extracted with chloroform, which dissolves the glucoside, which can then be crystallized out.

The first successful synthesis of a natural glucoside was accomplished by Arthur Michael in 1879, who caused acetochlorhydrose (obtained by the action of acetyl chloride upon glucose) to act upon the potassium compound of salicyl-aldehyde in alcoholic solution, when helicin was formed, and this, by the action of sodium amalgam, was converted into salicin. The same synthesis led to the formation of populin (benzoyl-salicin), and the corresponding reaction of acetochlorhydrose upon the potassium compound of methyl-hydroquinone led to the synthesis of methyl-arbutin, another naturally occurring glucoside. A newer and much more generally applicable method for the synthesis of the glucosides has been recently announced[1] by Emil Fischer. He finds when glucose and other sugars of the monosaccharide class (see p. 633) are dissolved in an alcohol, and hydrochloric acid gas is passed in, there forms a glucoside or mixed ether with the elimination of water. This reaction seems to be available for all the alcohols; in the case of glucose it has been proved with methyl, ethyl, propyl, isopropyl, amyl, allyl, and benzyl alcohols, as also with ethylene glycol and glycerin. It may even be employed for the hydroxy-acids (alcohol-acids), as was proved by the preparation of lactic glucoside. Where the sugar is completely insoluble in the alcohol, which is the case with many compounds of the aromatic and terpene series, in place of glucose, acetochlorhydrose, or pentacetyl-glucose, may be employed, as both are soluble in ether, benzene, and chloroform. As the bioses (cane- and milk-sugar and maltose) are hydrolyzed by hydrochloric acid, they cannot be converted in this way into glucoside-like compounds. These new artificial glucosides, like the natural ones, are unattacked by boiling alkalies, Fehling's solution and phenyl-hydrazine ; if, however, they be heated with dilute acids they are readily hydrolyzed into their components. They are likewise hydrolyzed by the invertase of yeast.

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[1] Berichte der Che [illegible] 2400.

The glucosides which are of more especial pharmaceutical or medical importance are the following :

Amygdalin, $C_{20}H_{27}NO_{11}.3H_2O$, is found in bitter almonds and in the kernels of fruit. It is extracted by alcohol from the compacted cake of the almond after the oil has been pressed out. It forms a white, crystalline powder, of slightly bitter taste, melting at 200°. When boiled with dilute acids, or when the aqueous extract of the bitter almond is digested at 25°–35°, it is decomposed according to the reaction :

$$C_{20}H_{27}NO_{11} + 2H_2O = C_7H_6O + CNH + 2C_6H_{12}O_6,$$

the products being benzaldehyde, hydrocyanic acid, and dextrose. In the latter case the decomposition is brought about by the *emulsin*, or soluble ferment, which occurs in both the sweet and the bitter almond.

Æsculin, $C_{15}H_{16}O_9.1\frac{1}{2}H_2O$, is found in the bark of the horse-chestnut. It forms prisms of a bitter taste, melting at 160°, and is decomposed by boiling with dilute acids or by emulsin into ***glucose*** and ***æsculetin*** (dioxycoumarin) :

$$C_{15}H_{16}O_9 + H_2O = C_6H_{12}O_6 + C_9H_6O_4.$$

Arbutin, $C_{12}H_{16}O_7.\frac{1}{2}H_2O$, and ***Methyl-arbutin***, $C_{13}H_{18}O_7$, are contained in *Arbutus Uva-ursi* and *Chimaphila umbellata* and other ericaceous plants. Both are bitter, crystallizable principles, separable only with difficulty. Both are decomposed by dilute acids or emulsin, the former into glucose and hydroquinone, and the latter into glucose and methyl-hydroquinone.

Carminic Acid, $C_{17}H_{18}O_{10}$, is the coloring constituent of cochineal (the dried female insect *Coccus cacti*), and the essential constituent of the commercial "carmine," obtained by extracting the cochineal with water and precipitating with alum. It is an amorphous, purplish-red mass, soluble in water and alcohol, which on boiling with dilute acids is decomposed as follows :

$$C_{17}H_{18}O_{10} + 2H_2O = \underset{\textbf{Carmine-red.}}{C_{11}H_{12}O_7} + \underset{\textbf{Carmine-sugar.}}{C_6H_{10}O_5}.$$

The salt is obtained in yellowish scales, the free glycyrrhizic acid in a gelatinous mass. It is decomposed on boiling with acids into *glycyrrhetin*, $C_{32}H_{47}NO_4$, and *parasaccharic acid*, $C_6H_{10}O_8$.

Helicin, $C_{13}H_{16}O_7$, is an oxidation product of salicin. It is split up by the action of dilute acids or emulsin into salicylic aldehyde, $C_6H_4\left\{\begin{matrix}OH\\COH\end{matrix}\right.$, and dextrose, $C_6H_{12}O_6$. Its synthesis by Michael has already been described.

Helleborin, $C_{36}H_{42}O_6$, and *Helleboreïn*, $C_{26}H_{44}O_{15}$, are glucosides occurring in the roots of black hellebore (*Helleborus niger*) and green hellebore (*H. viridis*).

Indican, $C_{26}H_{31}NO_{17}$, is a glucoside found in woad (*Isatis tinctoria*). It is decomposed by heating with dilute acids into *indiglucin*, $C_6H_{10}O_6$, and indigo-blue, C_8H_5NO. The reaction, however, is not a complete one, as other side-products are obtained. The so-called "indican" found in the urine at times is indoxylsulphuric acid (see p. 738).

Myronic Acid, $C_{10}H_{19}NS_2O_{10}$, is found in black mustard-seed as the potassium salt. The free acid is unstable. The potassium salt is decomposed by a ferment, *myrosin*, which is found mainly in the white mustard-seeds, according to the reaction:

$$C_{10}H_{18}NS_2O_{10}K = C_6H_{12}O_6 + KHSO_4 + C_3H_5.NCS,$$

the products being dextrose, acid potassium sulphate, and allylsulphocyanate (mustard oil).

Phloridzin, $C_{21}H_{24}O_{10}.2H_2O$, is a glucoside found in the root-bark of the apple-, pear-, plum-, and cherry-tree. It forms silky needles, fusing at 106°–108°. It is decomposed by dilute acids into glucose and *phloretin*, $C_{15}H_{14}O_5$. This latter decomposition product appears to occur also ready formed in the root-bark of the apple-tree.

Populin, $C_{20}H_{22}O_8$ or $C_{13}H_{17}(C_6H_5CO)O_7$, is benzoyl-salicin, and is found along with salicin in the bark and leaves of *Populus tremula*. When heated with dilute mineral acids it is split into glucose, benzoic acid, and saligenin. It is made synthetically from salicin by treatment with benzoyl-chloride.

Quercitrin, $C_{36}H_{38}O_{20}.3H_2O$, is a glucoside contained as the coloring principle of quercitron bark (from *Quercus tinctoria*). When boiled with dilute acids it splits up into *quercetin*, $C_{24}H_{16}O_{11}$, and *isodulcite*, $C_6H_{14}O_6$.

Ruberythric Acid, $C_{26}H_{28}O_{14}$, is the constituent of the madder-root, which by its decomposition yields alizarine, the reaction being:

$$C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6.$$

tilled with zinc-dust it yields anthracene. The benzene
tion of aloin, when heated with ammonia, gives a violet-red

Bixin, $C_{28}H_{34}O_5$, is obtained from "orlean," the fruit of
orellana. It forms reddish scales melting at 175°–176°.
still extensively used in dyeing, as it colors animal and veg
fibres yellow without the aid of mordants. It is also well
under the name of "annatto" in its use in butter color a
coloring of cheese.

Brasilin, $C_{16}H_{14}O_5$, is obtained from Brazil wood (*Peltop*
dubium). It forms amber-yellow crystals, which disso
alkalies with carmine color. When fused with potassium h
it yields resorcin. It is also used extensively in dyeing o
and cotton.

Cantharidin, $C_{10}H_{12}O_4$, is found in Spanish flies (*Lytta vesica*
It forms tablets melting at 218°. When heated with phosphorus
sulphide it yields *o*-xylol. When cantharidin is heated with alk
takes up the elements of water and forms *cantharidic acid*, $C_{10}H_{14}$
unstable acid, the potassium salt of which is used in medicine.

Chlorophyll is the name given to the green coloring mat
fresh vegetation. It appears to be a mixture of a yellow co
matter, *xanthophyll*, and a blue coloring matter, *cyanophyl*
crystalline product is also obtained, *chlorophyllan*, whic
reduction with zinc-dust yields the original chlorophyll.

Coloïn, $C_{22}H_{18}O_6$, is obtained from the coto bark of Bolivia.
pale-yellow crystals melting at 130°. When fused with caustic
or heated with concentrated hydrochloric acid to 140°, benzoic
split off.

Cubebin, $C_{10}H_{10}O_3$, is obtained from cubeb, the unripe fruit of
Cubeba. It forms small needles melting at 125°. When oxidiz
nitric acid it yields oxalic and picric acids; when fused with causti
ash it yields acetic and protocatechuic acids.

Curcumin, $C_{14}H_{14}O_4$, is the coloring principle of the tur
root (*Curcuma tinctoria*). It forms yellow prisms melti
178°. It is changed to a reddish-brown by alkalies, when
use as an indicator for alkalies. It is used somewhat for d
in compound colors.

Biliary Pigments.—In the bile and biliary calculi are
several pigments of definite composition. The best know
bilirubin, $C_{16}H_{18}N_2O_3$; *biliverdin*, $C_{16}H_{18}N_2O_4$; *bilifu*
$C_{16}H_{20}N_2O_4$; and *biliprasin*, $C_{16}H_{22}N_2O_6$. These biliary
ments may be recognized by Gmelin's test, in which nitric
containing nitrous acid is added, when colors changing

CHAPTER XI.

TISSUE-FORMING SUBSTANCES, OR PROTEID M

WHILE it was stated in the beginning of our disc
organic compounds (see p. 537) that the distinction
organic bodies (those produced in connection with the
of life) and *inorganic* bodies (those found in the mineral
or formed from mineral matter) no longer existed, no
was made of *organized* tissue. The living plant or a
matter how elementary its structure, is largely compose
of which the invariable organic constituents are prot
plant tissue the proteids share their importance with
and its alteration products, but in the animal tissue th
fundamentally important that it has well been said "
are indispensable constituents of every living, activ
tissue, and indissolubly connected with every manifes
animal activity."

The proteids of the animal body all come, directly
rectly, from vegetable sources, the nitrogenous or pro
ciples of which form an important element in our food.
action of certain ferments present in the alimentary juice
all proteids are capable of being converted into clo
bodies called peptones, which, after absorption, are c
reconversion into proteids. Not all the proteids of th
so reconverted, however, or go to the building up o
proteid tissues and organs; much undergoes decomposi
ducing carbon dioxide, water, and simpler nitrogen c
like urea, $CO(NH_2)_2$.

The various proteids are highly complex compound
high molecular weight and unknown constitution, c
carbon, hydrogen, oxygen, nitrogen, and sulphur, and
cases phosphorus and iron, in percentage compositio
within the following limits:

C.	H.	N.	S.	O.
From 50.6 per cent . .	6.9	15.2	0.3	20.9
to 54.5 " . . .	7.3	17.6	2.2	23.5

In addition to these constituents, the proteids, no ma peptones; with other proteids heat must be applied. It is known as the "Biuret reaction." If albumen is precipitated with alcohol and washed with ether, it gives a deep violet color when heated with hydrochloric acid. This is "Liebermann's reaction."

III. PRODUCTS OF DECOMPOSITION AND DIGESTIVE ACTION ON PROTEIDS.

1. **Action of Heat alone.**—When submitted to dry distillation the proteids yield the product known as Dippel's oil (see p. 748), which contains ammonium salts of the fatty acids, like butyric, valeric, and caproic, amines of the radicals of the paraffin series like methylamine, etc., aromatic compounds like aniline and phenol, and, lastly, the pyridine and quinoline bases.

2. **Action of Oxidizing Agents.**—Manganese dioxide and sulphuric acid or potassium bichromate and sulphuric acid acting upon the proteids produce cyanides, aldehydes, and acids of both the aromatic and the fatty groups. Nitric acid, as before stated, produces at first xanthoproteic acid, and by continued action oxybenzoic and paraoxybenzoic acids. Chlorine acting upon proteids produces, among other products, fumaric and oxalic acids. Bromine and water, when heated with proteids under pressure, cause the formation of carbon dioxide, aspartic, oxalic, and bromacetic acids, leucine, bromoform, bromanil, and other products.

3. **Action of Strong Acids and Caustic Alkalies.**—Prolonged boiling with sulphuric and hydrochloric acid, and fusion with caustic alkalies, give rise to practically the same products, among which are ammonia, acetic and valeric acids, amido-acids like leucine (see p. 604) and tyrosine, and indol and skatol (see p. 730).

4. **Action of Dilute Mineral Acids.**—Under the influence of dilute sulphuric acid (or hydrochloric acid in the presence of stannous chloride) hydrolysis ensues and a variety of products are obtained. Among these we have belonging to the class of methane derivatives leucine, aspartic acid, glutanic acid, and furfurol, and to the class of benzene derivatives tyrosine (see p. 725) and phenyl-amido-propionic acid.

5. **Decomposition under the Influence of Putrefactive Ferments.**—Reference was made to the decomposition of albuminoid matter under the influence of bacteria (see p. 655). The first effect on the albuminoids is a peptonization and then a

formation of products such as have been just mentioned under the two preceding cases of decomposition. In this case ammonia and hydrogen sulphide are also among the products of decomposition. In the putrefaction of gelatin or glue, instead of tyrosine, we have glycocoll as the product. Under certain pathological conditions this putrefactive change of albuminoids may take place in the intestines.

6. **Digestive Action on Proteids.**—In general, the effect of digestive action is to change proteids under the influence of enzymes into albumoses and peptones. In the digestive action of the stomach little true peptone is formed, but much albumose, while in the action of the pancreas the opposite result takes place. Very energetic action of the pancreatic ferment (see p. 652) changes the hemipeptones still further into amido-acids like tyrosine and leucine.

CLASSIFICATION OF PROTEID COMPOUNDS.

As the constitution of these compounds is still so entirely obscure, it is not possible to establish more than a provisional grouping of them. The scheme generally accepted by the best authorities is as follows:

I. **True Albuminoids,** including: 1, *Albumens;* 2, *Globulins;* 3, *Alkali-albuminates and Acid-albuminates;* 4, *Coagulated Albuminoids;* 5, *Albumoses and Peptones.*

II. **Nucleo-albumens.**

III. **Proteids,** including: 1, *Glucoproteids* (*a*, *Mucins ond Mucoids*, and *β*, *Hyalogens*); 2, *Chromoproteids* (*Hæmoglobins*).

IV. **Gelatinoids,** including: 1, *Keratins;* 2, *Collagen and Glue;* 3, *Elastin;* and 4, *Amyloid* (*Lardacein*).

I. TRUE ALBUMINOIDS.

These are free from phosphorus or contain it as calcium phosphate only; are readily peptonized (with the exception of the peptones, of course); yield, when decomposed by acids or allowed to putrify, amido-acids; soluble in dilute alkalies and acids (with the exception of the coagulated albuminoids). They occur in animal and vegetable tissues and liquid secretions.

1. **Albumens.**—These are soluble in water, dilute acids, and alkalies. The aqueous solution coagulates on heating in case neutral salts like sodium chloride or magnesium sulphate are present. If freed from salts (by precipitation of the insoluble

copper compound and treatment of this with strong pc hydrate) they do not coagulate on boiling. The soluti be completely precipitated by saturating it with ammoni phate or with sodium chloride followed by acetic ac varieties of this class we may mention :

Serum Albumen occurring in the blood, chyle, and Its solutions show a specific rotatory power of —56°, coagulable at temperatures of from 50° to 90°, accordin solvent.

Egg Albumen is found in the white of egg. Its speci tory power is —35.5°, and its temperature of coagulatio 56°. White of egg contains about 12 per cent. of album may be evaporated in thin films at ordinary temperatures losing its transparency or solubility in water.

Muscle Albumen exists in several varieties, coagula about 47°.

Milk Albumen (lactalbumen) is found in the milk of animals in amount from 0.5 to 1 per cent., and remains whey after the coagulation of the casein by rennet. I of coagulation ranges from 72° to 84°.

2. **Globulins.**—These are insoluble in water, but so dilute solutions of salts like sodium chloride, ammoniu ride, and sodium sulphate. The solutions coagulate on and are completely precipitated by saturation with am sulphate. With the exception of vitellin, they are prec by saturating the solution with common salt. As vari have :

Vitellin.—Obtained from the yolk of egg (**Vitellus,** L by extracting the fats and cholesterin with ether, dissolv white residue in common salt solution, and, after filtrati cipitating by the addition of water. It is difficult to free the lecithine which accompanies it in the egg yolk. It co at about 75° and is lævo-rotatory.

Plant vitellins are also obtained from beans, peas, almonc mustard, and corn. The aleurone grains, obtained from Brazil- other sources, seem to represent a crystalline albuminoid or a cc of an albuminoid with magnesia.

Crystallin, from the crystalline lens of the eye, is probably with vitellin.

Myosin is the product of the clotting of muscle plasma. It cc in 10 per cent. sodium chloride solution at 55°–56°. The subs the plasma generating the myosin is called *myosinogen.*

Plant myosins are also found in vegetable protoplasm.

Fibrinogen is found in blood plasma, in chyle, lymph, and serous fluids, and at times in transudations. In the clotting of blood it is converted into *fibrin*. This change takes place under the influence of a soluble fibrin ferment acting in the presence of neutral salts. It coagulates in 10 per cent. salt solution at 55°.

Serum Globulin (Paraglobulin or Fibrino-plastin) is found in blood plasma and blood serum, as well as in chyle, lymph, and serous fluids. It is incompletely precipitated by saturating the fluid with common salt. Its temperature of coagulation when in 10 per cent. sodium chloride solution is 75°.

3. Alkali-albuminates and Acid-albuminates.—Albuminoids are converted more or less rapidly by the action of alkalies and acids into the two classes above named.

The acid albuminates form jelly-like masses which, while not readily soluble in pure water, dissolve easily in acidified water. These acid solutions do not coagulate on boiling, but are precipitated by neutralization or adding neutral salts to the solution.

Syntonin is an acid albuminate prepared by the action of 0.1 per cent. hydrochloric acid upon muscle globulin. Frequently the whole class of acid albuminates are termed "syntonins."

The alkali-albuminates are not mere solutions of the albuminoids in alkali, but show a difference in percentage composition from the albuminoids from which they have been formed. This is because the alkali acts upon the albuminoid sufficiently to cause a splitting off of the nitrogen as ammonia and a loss of sulphur due to the formation of alkali sulphide.

Lieberkühn's Alkali-albuminate is a gelatinous mass insoluble in pure water, but soluble in dilute alkalies, which is obtained by the action of strong potassium hydrate solution upon egg albumen.

4. Coagulated Albuminoids.—These are formed by heating the neutral or slightly acid solutions of albumens and globulins. Prolonged action of strong alcohol also causes coagulation of proteids. The coagulated albuminoids are insoluble in water, dilute acids, and alkalies. By the action of the gastric or the pancreatic juice they are converted into peptones at the temperature of the body, and then go into solution. The coagulation of albuminoids must be distinguished from precipitation by neutralization or the addition of salts. In the latter case the precipitate still retains the properties possessed by the body when in solution; in the case of coagulation it is no longer capable of being changed back into the original proteid material.

Fibrin is formed by the action of the fibrin ferment upon fibrinogen (see p. 809). It is a white, elastic solid made up of fibre bundles.

Gluten results probably by the action of an enzyme (the gluten ferment) upon the globulin material of the flour. Gluten is, however, believed to be a mixture of *gluten-fibrin*, *gliadin* (vegetable glue), and *mucedin*.

5. **Albumoses and Peptones.**—Pepsin (see p. 652) in dilute hydrochloric acid solution and trypsin (see p. 651) in alkaline solution both have the power of "peptonizing" proteids. If the peptone solution so obtained be freed from unchanged albumen by coagulation and neutralization, we can in the filtrate precipitate the albumoses by saturating with ammonium sulphate, while the peptones will remain in solution. The albumoses are probably the first products of the action of enzymes upon proteids, and the continuance of the action changes them into peptones. Besides the difference in solubility in ammonium sulphate just stated, we may distinguish between the two classes also by the addition of potassium ferrocyanide to the acetic acid solution, albumoses being precipitated and peptones not, or the addition of common salt to saturation of the acetic acid solution, when albumoses are precipitated while peptones are not. At least two kinds of albumoses are to be distinguished: *anti-albumose* and *hemi-albumose*, to each of which corresponds a peptone, named therefore *anti-peptone* and *hemi-peptone* respectively. The first of these peptones cannot be further changed, while the latter (hemi-peptone) is changed by trypsin into leucine and tyrosine.

As already stated (see p. 804), the peptones, after absorption into the blood, are capable of reconversion into proteids or tissue-forming material.

The formation of poisonous albumoses, or "toxalbumens" as a product of decomposition of proteid matter in the body has already been referred to (see p. 776).

II. NUCLEO-ALBUMENS.

These contain phosphorus, and, at times, also iron. They are decomposed by artificial digestion with pepsin into peptones and *nucleïns*.

1. **Vitellin**, previously described under the globulins, may belong here, as by the pepsin digestion a nucleïn is separated from it.

2. **Casein** is found only in the milk of mammalia. It is insoluble in water, soluble in dilute alkali and in an excess of

hydrochloric or sulphuric acid. The caseins of cow's milk and human milk show, however, slight differences of solubility, as well as in the appearance of the precipitate obtained by the addition of dilute acids.

Casein is not coagulated by heat alone, a film forming in this case. The ferment rennin (see p. 652), however, readily coagulates it in the presence of the accompanying calcium phosphate, as do gastric and pancreatic juice; but in milk freed from the salts normally present, rennin will not cause the formation of a curd.

The artificial digestive action of pepsin and hydrochloric acid decomposes casein at the temperature of the blood into peptone and nucleïn.

Other nucleo-albumens are found in the synovial fluid, in the kidneys, and in urine.

Nucleïns.—These are bodies containing phosphorus which are closely related to the albuminoids, and are either found in animal and vegetable cells, or are formed by the decomposition of nucleo-albumens under the influence of pepsin and hydrochloric acid. They are insoluble in alcohol and ether, scarcely soluble in water, but easily soluble in dilute alkalies. By boiling with alkalies they lose their phosphorus, which splits off as alkali phosphate. Dilute mineral acids split off at ordinary temperatures metaphosphoric acid from certain nucleïns, as in the yolk of egg and yeast. By boiling the nucleïn of yeast with dilute acids xanthine, hypoxanthine, and adenin (see p. 667) are formed.

III. PROTEIDS.

The proteids are broken up by appropriate reagents into albuminoids on the one hand, and non-albuminoid compounds (carbohydrates or coloring matters) on the other. They may therefore be divided into two classes, *Glucoproteids* and *Chromoproteids*.

1. Glucoproteids.—These yield on decomposition with dilute acids, along with albuminoids, reducing compounds of the class of carbohydrates, or substances easily convertible into reducing carbohydrates.

a. **Mucins and Mucoids.**—The mucins are precipitated from their solutions by acetic acid, and the precipitates so obtained are not soluble in excess of the precipitant. When boiled with dilute mineral acids they yield reducing substances. The solutions of the true mucins are ropy in character. Those glucoproteids which form ropy solutions but are not peptones; with other proteids heat must be applied. It is known as the "Biuret reaction." If albumen is precipitated with alcohol and washed with ether, it gives a deep violet color when heated with hydrochloric acid. This is "Liebermann's reaction."

III. PRODUCTS OF DECOMPOSITION AND DIGESTIVE ACTION ON PROTEIDS.

1. **Action of Heat alone.**—When submitted to dry distillation the proteids yield the product known as Dippel's oil (see p. 748), which contains ammonium salts of the fatty acids, like butyric, valeric, and caproic, amines of the radicals of the paraffin series like methylamine, etc., aromatic compounds like aniline and phenol, and, lastly, the pyridine and quinoline bases.

2. **Action of Oxidizing Agents.**—Manganese dioxide and sulphuric acid or potassium bichromate and sulphuric acid acting upon the proteids produce cyanides, aldehydes, and acids of both the aromatic and the fatty groups. Nitric acid, as before stated, produces at first xanthoproteic acid, and by continued action oxybenzoic and paraoxybenzoic acids. Chlorine acting upon proteids produces, among other products, fumaric and oxalic acids. Bromine and water, when heated with proteids under pressure, cause the formation of carbon dioxide, aspartic, oxalic, and bromacetic acids, leucine, bromoform, bromanil, and other products.

3. **Action of Strong Acids and Caustic Alkalies.**—Prolonged boiling with sulphuric and hydrochloric acid, and fusion with caustic alkalies, give rise to practically the same products, among which are ammonia, acetic and valeric acids, amido-acids like leucine (see p. 604) and tyrosine, and indol and skatol (see p. 739).

4. **Action of Dilute Mineral Acids.**—Under the influence of dilute sulphuric acid (or hydrochloric acid in the presence of stannous chloride) hydrolysis ensues and a variety of products are obtained. Among these we have belonging to the class of methane derivatives leucine, aspartic acid, glutanic acid, and furfurol, and to the class of benzene derivatives tyrosine (see p. 725) and phenyl-amido-propionic acid.

5. **Decomposition under the Influence of Putrefactive Ferments.**—Reference was made to the decomposition of albuminoid matter under the influence of bacteria (see p. 655). The first effect on the albuminoids is a peptonization and then a

formation of products such as have been just mentioned under the two preceding cases of decomposition. In this case ammonia and hydrogen sulphide are also among the products of decomposition. In the putrefaction of gelatin or glue, instead of tyrosine, we have glycocoll as the product. Under certain pathological conditions this putrefactive change of albuminoids may take place in the intestines.

6. **Digestive Action on Proteids.**—In general, the effect of digestive action is to change proteids under the influence of enzymes into albumoses and peptones. In the digestive action of the stomach little true peptone is formed, but much albumose, while in the action of the pancreas the opposite result takes place. Very energetic action of the pancreatic ferment (see p. 652) changes the hemipeptones still further into amido-acids like tyrosine and leucine.

CLASSIFICATION OF PROTEID COMPOUNDS.

As the constitution of these compounds is still so entirely obscure, it is not possible to establish more than a provisional grouping of them. The scheme generally accepted by the best authorities is as follows:

I. **True Albuminoids,** including: 1, *Albumens;* 2, *Globulins;* 3, *Alkali-albuminates and Acid-albuminates;* 4, *Coagulated Albuminoids;* 5, *Albumoses and Peptones.*

II. **Nucleo-albumens.**

III. **Proteids,** including: 1, *Glucoproteids* (α, *Mucins ond Mucoids*, and β, *Hyalogens*); 2, *Chromoproteids* (*Hæmoglobins*).

IV. **Gelatinoids,** including: 1, *Keratins;* 2, *Collagen and Glue;* 3, *Elastin;* and 4, *Amyloid* (*Lardacein*).

I. TRUE ALBUMINOIDS.

These are free from phosphorus or contain it as calcium phosphate only; are readily peptonized (with the exception of the peptones, of course); yield, when decomposed by acids or allowed to putrify, amido-acids; soluble in dilute alkalies and acids (with the exception of the coagulated albuminoids). They occur in animal and vegetable tissues and liquid secretions.

1. **Albumens.**—These are soluble in water, dilute acids, and alkalies. The aqueous solution coagulates on heating in case neutral salts like sodium chloride or magnesium sulphate are present. If freed from salts (by precipitation of the insoluble

copper compound and treatment of this with strong potassium hydrate) they do not coagulate on boiling. The solution may be completely precipitated by saturating it with ammonium sulphate or with sodium chloride followed by acetic acid. As varieties of this class we may mention:

Serum Albumen occurring in the blood, chyle, and lymph. Its solutions show a specific rotatory power of —56°, and are coagulable at temperatures of from 50° to 90°, according to the solvent.

Egg Albumen is found in the white of egg. Its specific rotatory power is —35.5°, and its temperature of coagulation about 56°. White of egg contains about 12 per cent. of albumen, and may be evaporated in thin films at ordinary temperatures without losing its transparency or solubility in water.

Muscle Albumen exists in several varieties, coagulating at about 47°.

Milk Albumen (lactalbumen) is found in the milk of various animals in amount from 0.5 to 1 per cent., and remains in the whey after the coagulation of the casein by rennet. Its point of coagulation ranges from 72° to 84°.

2. **Globulins.**—These are insoluble in water, but soluble in dilute solutions of salts like sodium chloride, ammonium chloride, and sodium sulphate. The solutions coagulate on boiling, and are completely precipitated by saturation with ammonium sulphate. With the exception of vitellin, they are precipitated by saturating the solution with common salt. As varieties we have:

Vitellin.—Obtained from the yolk of egg (**Vitellus,** U. S. P.) by extracting the fats and cholesterin with ether, dissolving the white residue in common salt solution, and, after filtration, precipitating by the addition of water. It is difficult to free it from the lecithine which accompanies it in the egg yolk. It coagulates at about 75° and is lævo-rotatory.

Plant vitellins are also obtained from beans, peas, almonds, white mustard, and corn. The aleurone grains, obtained from Brazil-nuts and other sources, seem to represent a crystalline albuminoid or a compound of an albuminoid with magnesia.

Crystallin, from the crystalline lens of the eye, is probably identical with vitellin.

Myosin is the product of the clotting of muscle plasma. It coagulates in 10 per cent. sodium chloride solution at 55°–56°. The substance in the plasma generating the myosin is called *myosinogen.*

Plant myosins are also found in vegetable protoplasm.

Fibrinogen is found in blood plasma, in chyle, lymph, and serous fluids, and at times in transudations. In the clotting of blood it is converted into *fibrin*. This change takes place under the influence of a soluble fibrin ferment acting in the presence of neutral salts. It coagulates in 10 per cent. salt solution at 55°.

Serum Globulin (Paraglobulin or Fibrino-plastin) is found in blood plasma and blood serum, as well as in chyle, lymph, and serous fluids. It is incompletely precipitated by saturating the fluid with common salt. Its temperature of coagulation when in 10 per cent. sodium chloride solution is 75°.

3. Alkali-albuminates and Acid-albuminates.—Albuminoids are converted more or less rapidly by the action of alkalies and acids into the two classes above named.

The acid albuminates form jelly-like masses which, while not readily soluble in pure water, dissolve easily in acidified water. These acid solutions do not coagulate on boiling, but are precipitated by neutralization or adding neutral salts to the solution.

Syntonin is an acid albuminate prepared by the action of 0.1 per cent. hydrochloric acid upon muscle globulin. Frequently the whole class of acid albuminates are termed "syntonins."

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β. **Hyalogens.**—These are little-investigated substances which are found in the skeletons of lower forms of animal life. By the action of alkalies they are changed into *hyalines*, from which, by more complete decomposition, reducing compounds (possibly carbohydrates) are obtained.

2. **Chromoproteids.**—These compounds break up into albumen and coloring matter. The most important representatives of this class are the *Hæmoglobins*, or coloring matters of the blood. The parent substance of these compounds is *Oxyhæmoglobin*, as the compound of hæmoglobin with oxygen which occurs in arterial blood is called. To prepare it defibrinated blood is treated with ten times its volume of a salt solution (made by adding 1 volume of saturated salt solution to 10 volumes of water). The blood-corpuscles which settle out are freed from the salt solution by pouring this off; 2 volumes of water are added, and it is then shaken with an equal amount of ether. The ethereal layer is poured off and the aqueous layer filtered. The filtrate is precipitated by the addition of ¼ its volume of alcohol, and allowed to stand at a temperature of —5°. The composition of the oxyhæmoglobin crystals from the blood of different animals varies slightly, but the average composition is expressed by the formula $C_{600}H_{960}N_{154}FeS_3O_{179}$. Oxyhæmoglobin obtained from the blood of man and the majority of the lower animals crystallizes in prisms or rhombic plates of a beautiful blood-red color. The crystals are soluble in water, and the solution, if not too concentrated, shows two absorption bands between the lines D and E of the spectrum, which are visible with a dilution of even $\frac{1}{10000}$. At a temperature of from 60° to 70° oxyhæmoglobin splits up into albumen and hæmatin. One molecule of oxygen is held loosely combined in oxyhæmoglobin, and is given off in a vacuum or may be displaced by inert gases like nitrogen. The resulting compound is *reduced hæmoglobin*, which is present in venous blood, and results also from the putrefactive decomposition of oxyhæmoglobin. Its aqueous solution shows a broad absorption band between D and E. Hæmoglobin, by absorption of oxygen in the lungs, is changed into oxyhæmoglobin. It also combines even more readily with certain other gases, such as carbon monoxide, nitrogen dioxide, and hydrogen cyanide. *Carbon-monoxide-hæmoglobin* is a compound of 1 molecule of CO and 1 molecule of

hæmoglobin. Its aqueous solution also shows absorption bands in the spectroscope which differ in position from those of oxyhæmoglobin, being nearer the violet end of the spectrum. It may also be distinguished from oxyhæmoglobin, according to Hoppe-Seyler's test, by adding an equal volume of sodium hydrate solution of 1.3 sp. gr. The carbon monoxide compound is changed hereby to a clear red color, while ordinary blood is changed to a brownish mass.

Hæmatin, $C_{34}H_{35}N_4FeO_5$, is the colored decomposition product of the hæmoglobin. It is formed by the action of acids upon the blood, and by the decomposition of hæmin by an alkali hydrate. It is an amorphous, brownish-black powder, insoluble in water, alcohol, and ether, easily soluble in alkalies. Its alkaline solution shows a single broad absorption band extending from between C and D to near E of the spectrum. The acid solution shows several narrow bands, instead of the broad band just mentioned. Hæmatin forms a crystalline hydrochlorate, $C_{34}H_{35}N_4FeO_5.HCl$, known as *Hæmin*. These crystals are often obtained in examining dried blood-spots. The dried matter supposed to be blood is warmed in a watch-crystal with common salt and glacial acetic acid. On evaporating the solution on a water-bath characteristic crystals of hæmin are obtained. Hæmin forms a crystalline powder of silky lustre and bluish-black color, which is insoluble in water, alcohol, and ether, but soluble in dilute alkali, acidified alcohol, and hot glacial acetic acid.

By the action of concentrated sulphuric acid upon hæmatin in the presence of oxygen is formed *hæmoporphyrin*, and, by the action of the same acid upon hæmatin in the absence of oxygen, *hæmatolin*, both of which substances are free from iron.

IV. GELATINOIDS.

We include here several groups of insoluble substances, which are attacked with difficulty by digestive ferments, and differ, therefore, from the other tissue-forming materials.

1. **Keratins** (or horny substances).—These compounds are found in the epithelial tissues, nails, hair, horns, and hoofs, and in feathers. They contain carbon, hydrogen, oxygen, nitrogen, and sulphur, the percentage of the last-named element varying considerably and being very loosely combined. These keratins are insoluble in water, alcohol, ether, dilute acids, and alkalies. They are hardly attacked by digestive ferments, but are decomposed by boiling with water under pressure, hydrogen sulphide

being evolved. When boiled with strong acids, leucine, tyrosin and aspartic acid are formed.

Keratin, when prepared from feathers, forms a brownish-yellc powder, soluble in concentrated acetic acid, alkalies, and ar monia, which has been recommended for coating pills, so as enable them to withstand the digestive liquids of the stomac and to act only when in the intestines.

Neurokeratin is a variety which has been isolated from the nerv and brain-tissue.

Spongin is the substance of the common bath-sponge. When decor posed by acids it yields tyrosine, leucine, and glycocoll.

Silk consists of *fibroïn*, $C_{15}H_{23}N_5O_6$, which is covered with a alteration product known as *sericin* (or silk-glue), $C_{15}H_{25}N_5O$ The latter is easily removed by warm soap-water, and its solutic so obtained constitutes the "boiled-off" liquor of the silk-dye Fibroïn is decomposed by acids, yielding glycocoll, alanine, leı cine, and tyrosine.

Cerebrin and *Chitin*, which may be included here, have already be described (see p. 799).

2. **Collagen.**—The white fibres of connective tissues (sinev and tendons) are mainly composed of a substance now general termed collagen. Its most important reaction is the change in *gelatin* when boiled with water. Bones also contain a substanc *ossein*, which undergoes a similar change. The solutions o tained in these cases "gelatinize" or set to a jelly-like mass c cooling, and this, if carefully dried, forms the commercial gelati or *glue*. Solutions of gelatin are precipitated by a number c the alkaloidal reagents (see p. 757). Pepsin or trypsin conver gelatin into gelatine-peptones, and certain micro-organisms hav also the power of liquefying and decomposing it. When decor posed by acids gelatin yields ammonia, glycocoll, leucine, ar glutamic acid, but not tyrosine or iodol.

Hoffmeister has found that by heating gelatin for some time t 130° it loses about 0·755 per cent. of water, and becomes cor verted into a body in all respects identical with collagen. H therefore considers that collagen is simply the anhydride of gela tin, and ascribes to them the formulas $C_{102}H_{151}N_{31}O_{39}$ for gelatir and $C_{102}H_{149}N_{31}O_{38}$ for collagen.

Chondrin, formerly considered to be the gelatigenous material of tis sues, is now considered to be a mixture of gelatin with chondromucoic and chondroitic acid.

3. **Elastin.**—When connective tissue is treated with acetic acid the white fibres swell up and become transparent, whilst the elastic fibres remain unaltered, and can be seen very distinctly. Prolonged boiling with water also decomposes the collagen of the white fibres and leaves the elastin. So far as is known elastin is not soluble in any liquid which does not decompose it. It is soluble in boiling potassium hydrate, in cold concentrated sulphuric acid, and in concentrated nitric acid. It is also gradually dissolved when digested with pepsin and trypsin. With sulphuric acid it yields leucine, but no tyrosine.

4. **Amyloid** (Lardaceïn) is a proteid substance found under pathological conditions in the liver, spleen, kidneys, and intestines. It forms small grains somewhat resembling starch granules, whence the name. It is acted upon by pepsin and hydrochloric acid with great difficulty. When dissolved in alkalies it yields an alkali-albuminate, and with concentrated hydrochloric acid yields an acid-albuminate. It is colored reddish-brown with iodine, and violet with iodine and sulphuric acid.

PART V.

ANALYTICAL CHEMISTRY AND PHARMACEUTICAL ASSAYING.

PART V.

ANALYTICAL CHEMISTRY AND PHARMACEUTICAL ASSAYING.

SECTION I.

QUALITATIVE ANALYSIS.

PRELIMINARY CONSIDERATIONS.

QUALITATIVE analysis may be appropriately considered under two heads, (1) the behavior of known elements and compounds towards certain other known elements and compounds, termed reagents, and (2) the separation or detection of unknown elements and compounds by means of these reagents. The latter is frequently accomplished by converting the element sought into some well-known and characteristic compound.

A reagent, then, is a substance applied to another in order to separate it, or to produce with it some distinguishing result.

Reagents may be applied in two ways, wet and dry ; the former usually consists in adding a solution of the reagent to a solution of the substance under investigation. This method of employing reagents is almost exclusively used in pharmaceutical analysis.

The list of reagents given in the United States Pharmacopœia will be found to supply all the needs for a full study of qualitative analysis.

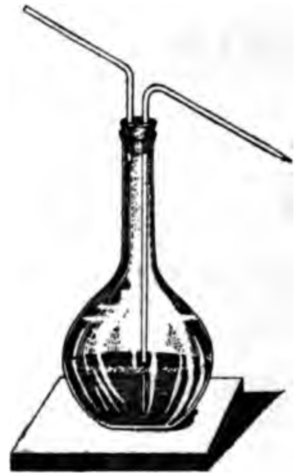
Precipitation is the process performed most frequently in chemical analysis. It consists in adding a reagent, drop by drop, to a solution of the substance under examination until, after agitating and sometimes warming, no further precipitate is produced.

Filtration is the natural sequence of precipitation, and is most readily accomplished by pouring the mixture on a plain filter,—

that is, one which has been folded twice and opened so as to form a cone; this cone should be placed in a funnel large enough t prevent the filter projecting above its edge.

The result of filtration is the separation of a mixture into *precipitate* and a *filtrate.* Filtration should not be performe immediately after the reagent h been added, but a few minutes should be allowed to elapse for complete precipitation to take place, and the filtrate should always be tested with a little more of the reagent in order to determine if the precipitation has been complete.

FIG. 106.



Wash-bottle.

Precipitates, as a rule, should be well washed; this is accomplished by the use of a wash-bottle, illustrated in Fig. 106. By blowing air into the shorter tube a jet of water is forced from the longer one, and this jet may be directed on any part of the precipitate. It sometimes prevents the washings from coming through cloudy to allow all of the liquid on the precipitate to drain through before adding more. In qualitative analysis it is not necessary to save all the washings.

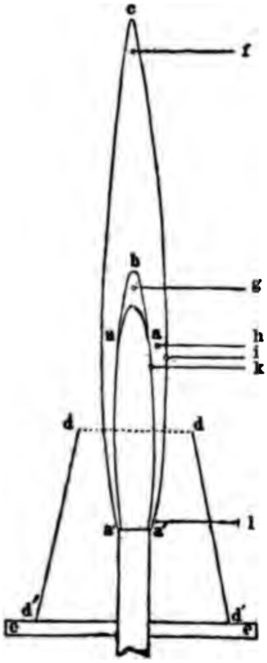
Reagents in the dry way are generally applied with the aid of heat. This is usually accomplished by heating the substance in a borax bead or on charcoal.

The process by which a color is imparted to the non-luminous flame of a Bunsen burner, when a substance on platinum wire is held therein, may also be considered to belong to this method. For treatment on charcoal a blowpipe is necessary, but borax beads may be sufficiently heated in the Bunsen burner flame. To fully describe the structure of this flame, Fig. 107 is here given. The inner cone terminates at or near a a, the flame envelope extends from a' a' to c; f is the upper oxidizing flame, g is the upper reducing flame, and is in the luminous part a a b, b is the point of highest temperature, i is the lower oxidizing flame, k is the lower reducing flame, and l is the base of the flame.

The blowpipe flame is best illustrated by Fig. 108, in which a is the reducing flame, and b the point of most energetic oxidation.

The flame reactions are best obtained by use of the platinum wire which is conveniently attached to a glass handle, as shown in Fig. 109. This wire, with some of the substance adhering to it, should be brought into the flame a little above the base, *l*, Fig. 107. That part of the wire nearest the glass handle should be introduced first, and the wire drawn through to the loop at the end. In this way the substance is volatilized and imparts color to the whole length of the flame from *l* to *c*. To clean the wire it should be alternately dipped in distilled water and drawn through the flame at *g*.

FIG. 107.



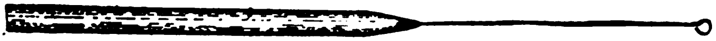
Gas flame.

FIG. 108.

Blowpipe flame.

Analytical chemistry should be studied with the assistance of a competent instructor whenever that is possible. To those, however, who may be under the necessity of undertaking the study alone some simple directions may be useful.

FIG. 109.



Platinum wire.

In order to separate and detect the different elements, one should first make a practical study of them and their behavior towards reagents.

In commencing the analysis of the first group, therefore, the action of a few reagents should be tried on a salt of potassium preferably the chloride. In other words, the student should perform the reactions given under potassium, sodium, lithium and ammonium, as described in the text. Having acquired a thorough knowledge of the behavior of the salts of these elements towards certain reagents, he is prepared to try the same reagents on unknown solutions containing salts of this group. He should have some one else to furnish him with these solutions, so that he may be literally working on unknown substances. When the material taken for analysis is in the form of a liquid it is usually described as the *original solution.*

After a thorough knowledge of the first group has been acquired, which may usually be accomplished by the analysis of from three to five unknown solutions, the student is prepared to undertake the study of the second group. This is done, as with the first group, by performing the reactions with known solutions, and then detecting unknown bases. When the second group is completed, a number of solutions containing salts of both groups should be analyzed. In this way one group is added at a time until the seven groups of bases have been studied. The acids are then taken up in like manner, and, finally, unknown substances are examined for both bases and acids.

It is still more important that the student should be under the guidance of a competent instructor when he commences the study of quantitative analysis.

The most important rules to be observed in the practical study of chemistry are: to avoid all feverish hurry; to add no reagent until time has been taken to understand the purpose for which it is added; to remove from the table, as soon as any part of an operation is completed, the materials concerned in it; to clean the vessels in which the substances were contained; to observe the strictest care and neatness in all manipulations; and, finally, to keep a complete record of all observations made and work performed.

CHAPTER I.

THE REACTIONS AND DETECTION OF BASES.

Group I. Potassium, Sodium, Lithium, Ammonium.

REACTIONS OF SOLUBLE SALTS OF POTASSIUM.

Use a 5-per-cent. solution of potassium chloride, KCl.

1. $PtCl_4$ added to some of the above solution of KCl causes a yellow, crystalline precipitate of **potassium platinic chloride**, K_2PtCl_6,* soluble in excess of water.

$$2KCl + PtCl_4 = K_2PtCl_6.$$

2. $Co_2(NO_2)_6 6NaNO_2$ produces in neutral or slightly acid solutions a yellow, crystalline precipitate of **potassium cobaltic nitrite**, $K_6Co_2(NO_2)_{12}$.

$$6KCl + Co_2(NO_2)_6 6NaNO_2 = K_6Co_2(NO_2)_{12} + 6NaCl.$$

Alkaline solutions should be acidified with acetic acid previous to adding the reagent.

3. $H_2C_4H_4O_6$, in concentrated solution, added to a solution of a salt of potassium, produces a white, crystalline precipitate of **acid potassium tartrate**, $KHC_4H_4O_6$, soluble in excess of water, readily in hot water, acids, or potassium hydrate.

$$KCl + H_2C_4H_4O_6 = KHC_4H_4O_6 + HCl.$$

4. $C_6H_2(NO_2)_3OH$, in saturated solution, forms a yellow, crystalline precipitate of **potassium picrate**, $C_6H_2(NO_2)_3OK$

$$KCl + C_6H_2(NO_2)_3OH = C_6H_2(NO_2)_3OK + HCl.$$

5. A fragment of a potassium salt, on the loop of a platinum wire held in the non-luminous flame of a Bunsen gas-lamp, imparts a **violet** color. Organic matter also colors the flame violet; hence it should be removed by ignition before testing for potassium. This reaction is also interfered with by the presence of sodium salts, which color the flame yellow. The yellow rays

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* Agitation by stirring with a glass rod facilitates the formation of this and the following precipitates of this element, while the addition of alcohol serves to render the precipitation more complete. The precipitates from the several reactions under potassium should be preserved to compare with tho[illegible]tained from ammonium, that the great similarity may be noted.

of sodium may be excluded by viewing the flame throu glass.

6. Potassium salts are not volatile at a low red heat, slowly volatilized at a white heat.

REACTIONS OF SOLUBLE SALTS OF SODIUM.

Use a 1-per-cent. solution of sodium chloride, NaCl.

1. Sodium salts color the non-luminous flame **yellow.**

So delicate is this reaction that the merest traces of the are revealed by it, and even the presence of much larger ties of potassium salts do not render it less effective.

It is particularly characteristic of these yellow rays th do not pass through a blue medium ; consequently, in th cation of the flame test, the yellow color may be exclu viewing the flame through a blue glass (tinted with cobalt which thus serves to render the violet color imparted by sium salts still more distinct.

2. The salts of sodium are not volatile at a low red h are slowly volatilized at a white heat.

REACTIONS OF SOLUBLE SALTS OF LITHIUM.

Use a 2-per-cent. solution of lithium chloride, LiCl.

1. Na_2HPO_4 produces, on boiling, a white precipitate **ium phosphate,** Li_3PO_4.

$$3LiCl + Na_2HPO_4 = Li_3PO_4 + 2NaCl + HC$$

This reaction takes place more readily when the solutio made alkaline with NaOH or NH_4OH.

2. Lithium salts impart an intense **crimson** color to t luminous flame. This is more or less interfered with by salts, but the yellow color of sodium may be excluded b **nary** blue glass, which, if not too dark, will allow the c rays of lithium to pass through. These must not be c with the violet potassium rays, which will pass through blue glass.

3. Lithium salts are not volatile at a low red heat, slowly volatilized at a white heat.

REACTIONS OF SOLUBLE SALTS OF AMMONIUM.

Use a 5-per-cent. solution of ammonium chloride, NH_4C

1. $PtCl_4$ produces a yellow, crystalline precipitate of **a nium platinic chloride,** $(NH_4)_2PtCl_6$.

Precipitate Li.	Filtrate K.
WHITE. Wash with hot water containing NH_4OH until the washings show no more yellow flame from sodium salts, then dissolve the ppt. in HCl and apply flame test. Crimson color indicates Li.	Acidify with $HC_2H_3O_2$, and add $Co_2(NO_2)_6 6NaNO_2$. Yellow ppt. indicates K.

Group II. Barium, Strontium, Calcium, Magnesium.

REACTIONS OF SOLUBLE SALTS OF BARIUM.

Use a 5-per-cent. solution of barium chloride, $BaCl_2.2H_2O$.

1. H_2SO_4 produces an immediate precipitation of white **barium sulphate**, $BaSO_4$, insoluble in boiling HCl or HNO_3.

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl.$$

2. K_2CrO_4, even in dilute solutions, causes a yellow precipitate of **barium chromate**, $BaCrO_4$, soluble in HCl or HNO_3, but insoluble in $HC_2H_3O_2$.

$$BaCl_2 + K_2CrO_4 = BaCrO_4 + 2KCl.$$

3. $(NH_4)_2CO_3$ precipitates white **barium carbonate**, $BaCO_3$, soluble in $HC_2H_3O_2$.

$$BaCl_2 + (NH_4)_2CO_3 = BaCO_3 + 2NH_4Cl.$$

4. $(NH_4)_2HPO_4$ produces a white precipitate of **barium phosphate**, $BaHPO_4$, soluble in $HC_2H_3O_2$ or HCl.

$$BaCl_2 + (NH_4)_2HPO_4 = BaHPO_4 + 2NH_4Cl.$$

5. $(NH_4)_2C_2O_4$ causes a white precipitate of **barium oxalate** BaC_2O_4, slightly soluble in $HC_2H_3O_2$. This precipitation will not take place in very dilute solutions.

$$BaCl_2 + (NH_4)_2C_2O_4 = BaC_2O_4 + 2NH_4Cl.$$

6. The salts of barium impart a **green** color to the non-luminous flame.

REACTIONS OF SOLUBLE SALTS OF STRONTIUM.

Use a 5-per-cent. solution of strontium nitrate, $Sr(NO_3)_2$.

1. H_2SO_4 forms a white precipitate of **strontium sulphate**, $SrSO_4$, immediately if the solution be strong, but not until after some time if it be very dilute.

2. K_2CrO_4 produces no precipitate in the presence of $HC_2H_3O_2$, but if the solution be made alkaline with KOH, a yellow precipitate of **strontium chromate**, $SrCrO_4$, falls.

PO_4, slightly soluble in water, but almost insoluble in water con- taining NH_4OH.

$$MgSO_4 + NH_4OH + (NH_4)_2HPO_4 = Mg(NH_4)PO_4 + (NH_4)_2SO_4 + H_2O.$$

Violent agitation or stirring assists in the formation of thi precipitate.

$(NH_4)_2HAsO_4$, under similar circumstances, forms white, crys- talline **magnesium ammonium arsenate,** $Mg(NH_4)AsO_4$.

NH_4Cl takes no part in the reaction, except to prevent the precipitation of $Mg(OH)_2$.

4. The salts of magnesium do not impart color to the flame.

Chart for the Detection of the Bases in a Solutio containing Soluble Salts of Group II.

<table>
<tr><td colspan="4">Add to the original solution NH_4Cl, NH_4OH, and $(NH_4)_2CO_3$, boil and filter.</td></tr>
<tr><td colspan="3">Precipitate Ba, Sr, Ca.
Wash, dissolve in $HC_2H_3O_2$, dilute with H_2O, add K_2CrO_4, and filter.</td><td rowspan="3">Filtrate Mg.
Allow to cool, ad $(NH_4)_2HPO_4$, and agitate. White, crystalline ppt. indicates Mg.</td></tr>
<tr><td rowspan="2">Ppt. Ba.
Yellow.</td><td colspan="2">Filtrate Sr, Ca.
Add very dilute H_2SO_4, allow to stand for 10 minutes, and filter.</td></tr>
<tr><td>Ppt. Sr.
White.
Wash, moisten with HCl, and confirm by flame test.</td><td>Filtrate Ca.
Add NH_4OH in excess and $(NH_4)_2C_2O_4$. White precipitate indicates Ca.</td></tr>
</table>

That the student may become acquainted with the method of analysis by this and subsequent charts the following explanation is given, in the belief that a thorough study of it will enable him to understand all the charts which follow, as they are simply enlargements of this scheme.

To a convenient quantity of the original solution in a test-tube add an equal volume of a 10-per-cent. solution of NH_4Cl, close and invert the tube so as to thoroughly mix the contents, add NH_4OH in excess (or until, after mixing, the solution smells distinctly of it), then add $(NH_4)_2CO_3$, and, if a precipitate is formed, boil, and continue the addition of this reagent until the precipitation is completed, then filter.

We suppose all four of the bases under consideration to be present in the solution until their absence is proven; so by the foregoing treatment we separate them into two forms,—an insoluble part, called a *precipitate*, and consisting of Ba, Sr, and Ca as carbonates, and a liquid portion, called a *filtrate*, and containing Mg as carbonate, to keep which from precipitating the NH_4Cl is added.

A few drops more of $(NH_4)_2CO_3$ should be added to the filtrate and the whole again boiled, to make sure that all the carbonates of Ba, Sr, and Ca have been precipitated. If this is found to be the case, $(NH_4)_2HPO_4$ is added to the cooled filtrate, when, if Mg be present, a white, crystalline precipitate of $Mg(NH_4)PO_4$ will form.

The precipitate of the carbonates of Ba, Sr, and Ca, after being washed by forcing a jet of water from the wash-bottle on it, is dissolved in $HC_2H_3O_2$, which is distributed in drops upon the filter. Effervescence arises from the action of the $HC_2H_3O_2$ in decomposing the carbonates to form soluble acetates of Ba, Sr, and Ca. The solution so obtained is allowed to pass through the filter, which to prevent loss of material is afterwards washed with water; the latter being collected with the $HC_2H_3O_2$ solution, serves the additional purpose of diluting it.

To this solution a few drops of K_2CrO_4 are added. If Ba is present a yellow precipitate is produced, in which case sufficient of the K_2CrO_4 should be added to impart its yellow color to the supernatant liquid, thus signifying the complete precipitation of the Ba as $BaCrO_4$. The mixture is then filtered; this again divides the material into a precipitate and a filtrate, the former indicating Ba, and the latter containing Sr and Ca. To this filtrate very dilute H_2SO_4 (made by adding a small quantity of H_2SO_4 to about 20 times its volume of water) is added, the mixture allowed to stand for 10 minutes for the $SrSO_4$ to form and subside, and then filtered, whereby another precipitate, consisting of Sr as $SrSO_4$, and a filtrate containing the Ca are obtained.

The precipitate is washed well with water, then moistened with a drop of HCl (which serves to render it somewhat more volatile), and confirmed by holding it upon a platinum wire in the non-luminous flame, which will be colored intense red if Sr be present. To the filtrate from the $SrSO_4$ precipitate add NH_4OH in excess, and then $(NH_4)_2C_2O_4$, when, if the solution contained Ca, a white precipitate of CaC_2O_4 will be produced.

CHART FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF ALL THE FOREGOING ELEMENTS.

<table>
<tr><td colspan="6">**Ba, Sr, Ca, Mg, K, Na, Li, NH_4.**
Add to the original solution NH_4Cl, NH_4OH, and $(NH_4)_2CO_3$, boil and filter.</td></tr>
<tr><td colspan="3">**Precipitate Ba, Sr, Ca.**
Wash, dissolve in $HC_2H_3O_2$, dilute with H_2O, add K_2CrO_4, and filter.</td><td colspan="3">**Filtrate Mg, K, Na, Li, NH_4.**
Allow to cool, add $(NH_4)_2HPO_4$, agitate, and filter.</td></tr>
<tr><td rowspan="3">**Ppt. Ba.**
Yellow.</td><td colspan="2">**Filtrate Sr, Ca.**
Add very dilute H_2SO_4, allow to stand, and filter.</td><td rowspan="3">**Ppt. Mg.**
White, crystalline.</td><td colspan="2">**Filtrate K, Na, Li, NH_4.**
Add Na_2HPO_4 and NaOH, boil to a small bulk and until all NH_3 has been expelled, filter.</td></tr>
<tr><td rowspan="2">**Ppt. Sr.**
White. Confirm by flame test.</td><td rowspan="2">**Filtrate Ca.**
Add NH_4OH until alkaline, and then $(NH_4)_2C_2O_4$. White ppt.</td><td rowspan="2">**Ppt. Li.**
White. Confirm by flame test.</td><td>**Filtrate K, Na.**
Acidify with $HC_2H_3O_2$ and add $Co_2(NO_2)_6 \cdot 6NaNO_2$. Yellow ppt. indicates K.</td></tr>
<tr><td>Test for Na and NH_4 in the original solution.</td></tr>
</table>

Group III. Manganese, Zinc, Cobalt, Nickel.

REACTIONS OF SOLUBLE SALTS OF MANGANESE.

Use a 2-per-cent. solution of manganous sulphate, $MnSO_4 \cdot 4H_2O$.

1. NH_4HS, in neutral or alkaline solution, precipitates flesh-colored **manganous sulphide,** MnS, which on exposure to air becomes brown.

$$MnSO_4 + 2NH_4HS = MnS + (NH_4)_2SO_4 + H_2S.$$

When $NH_4C_2H_3O_2$ is present and NH_4HS or H_2S is added, MnS is formed, but is held in solution by the $HC_2H_3O_2$ set free in the reaction.

$$MnSO_4 + 2NH_4C_2H_3O_2 + H_2S = MnS + (NH_4)_2SO_4 + 2HC_2H_3O_2.$$

HCl or HNO_3 also dissolves the precipitate.

hydrate, $Zn(OH)_2$, readily soluble in excess of the reagent, forming **zincates,** as, for instance, $Zn(OK)_2$.

$$Zn(OH)_2 + 2KOH = Zn(OK)_2 + 2H_2O.$$

These compounds are decomposed on boiling, $Zn(OH)_2$ being again precipitated, or by NH_4HS, ZnS resulting.

4. $(NH_4)_2CO_3$ forms a white precipitate of **basic zinc carbonate,** $(ZnCO_3)_2(Zn(OH)_2)_3$, readily soluble in excess.

$$5ZnSO_4 + 5(NH_4)_2CO_3 + 3H_2O = (ZnCO_3)_2(Zn(OH)_2)_3 + 5(NH_4)_2SO_4 + 3CO_2.$$

5. K_2CO_3 or Na_2CO_3 produces the same precipitate, but does not redissolve it when added in excess.

6. On charcoal, before the blowpipe, metallic zinc volatilizes and burns, forming an incrustation of **zinc oxide,** ZnO, which is yellow while hot, but becomes white on cooling. If this coating be moistened with a drop of cobaltous nitrate, and again heated in the outer flame, it becomes green from the admixture with cobalt oxide.

REACTIONS OF SOLUBLE SALTS OF COBALT.

Use a 2-per-cent. solution of cobaltous nitrate, $Co(NO_3)_2 \cdot 6H_2O$.

1. H_2S, in the presence of $NH_4C_2H_3O_2$, produces a black precipitate of **cobaltous sulphide,** CoS, insoluble in $HC_2H_3O_2$ and cold dilute HCl, but soluble in hot HCl or HNO_3.

2. NH_4HS precipitates CoS. The precipitation is promoted by the presence of NH_4Cl.

3. KOH or NaOH produces a blue precipitate of **cobaltous hydrate,** $Co(OH)_2$, insoluble in excess, and becoming pink on boiling or exposure to air.

4. NH_4OH causes a precipitate of $Co(OH)_2$, soluble in excess of the reagent, with the production of a red color. Sugar and some other organic compounds prevent the precipitation by the alkali hydrates.

5. KCN gives a red-brown precipitate of **cobaltous cyanide,** $Co(CN)_2$.

$$Co(NO_3)_2 + 2KCN = Co(CN)_2 + 2KNO_3.$$

The precipitate dissolves in an excess of KCN to produce **cobaltous potassium cyanide,** $Co(CN)_2.4KCN$. From this solution $Co(CN)_2$ is again precipitated by HCl. If, however, the solution be boiled with only a few drops of HCl, $Co(CN)_2$

CHART FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP III.

<table>
<tr><td colspan="4">Add NH_4OH to the original solution until strongly alkaline, then acidify slightly with $HC_2H_3O_2$, warm, add H_2S until the liquid smells strongly of the reagent, and filter.</td></tr>
<tr><td colspan="3">Precipitate Zn, Co, Ni.
Wash, dissolve in a boiling-hot mixture of 2 parts HCl and 1 part HNO_3, evaporate almost to dryness, add H_2O and then KOH until distinctly alkaline, and filter.</td><td rowspan="3">Filtrate Mn.
Make alkaline with NH_4OH and add H_2S.
Flesh-colored ppt.
Apply Crum's test to the original solution.</td></tr>
<tr><td colspan="2">Precipitate, Co, Ni.
Wash, dissolve in hot HCl, evaporate almost to dryness, add H_2O and then KCN until the ppt. first formed redissolves, boil with a drop or two of HCl for one or two minutes, then add more HCl until the reaction is acid and boil until all odor of HCN disappears, make alkaline with KOH, and filter.</td><td rowspan="2">Filt. Zn.
Add NH_4HS, warm, and allow to stand.
White ppt.</td></tr>
<tr><td>Ppt. Ni.
Green.
Wash well, allow to drain, and test with borax bead.
Reddish-brown color.</td><td>Filtrate Co.
Evaporate to dryness and test with borax bead.
Blue color.</td></tr>
</table>

NOTES ON THE PRECEDING CHART.

1. Time and work may sometimes be saved by carefully noting the color of the precipitate produced by H_2S; for instance, if not black, Co and Ni are evidently absent.

2. The great delicacy of Crum's test for Mn when conducted under proper conditions recommends its invariable application to the original solution as the best means of detecting that element.

3. In evaporating the solution obtained by dissolving the precipitate in HCl and HNO_3 almost to dryness, precaution should be taken that the material is not overheated around the edge of the liquid and thus rendered partly insoluble in water. To obviate any such occurrence the application of heat should be discontinued when the solution has been reduced to some few drops; the dish should then be held in the fingers and rotated in such a manner that the evaporation of the remaining liquid shall be accomplished by the heat of the vessel.

FOREGOING ELEMENTS.

<table>
<tr><td colspan="10">Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH_4.
Add to the original solution NH_4Cl, NH_4OH and NH_4HS, warm * well and filter.</td></tr>
<tr><td colspan="4">Precipitate Mn, Zn, Co, Ni.
Wash, dissolve in HCl and HNO_3, evaporate almost to dryness, add H_2O and then NH_4OH until distinctly alkaline, acidify slightly with $HC_2H_3O_2$, warm, add H_2S, and filter.</td><td colspan="6">† Filtrate Ba, Sr, Ca, Mg, K, Na, Li, NH_4.
Evaporate to a small bulk or to dryness to remove NH_4HS, if necessary add H_2O, then add $(NH_4)_2CO_3$, boil and filter.</td></tr>
<tr><td colspan="3">Ppt. Zn, Co, Ni.
Wash, dissolve in HCl and HNO_3, evaporate almost to dryness, add H_2O and then KOH until distinctly alkaline, agitate and filter.</td><td rowspan="3">Filt. Mn.
Add NH_4OH until alkaline, and then H_2S. Flesh-colored precipitate. Apply Crum's test to the original solution.</td><td colspan="3">Ppt. Ba, Sr, Ca.
Wash, dissolve in $HC_2H_3O_2$, add H_2O and then K_2CrO_4, filter.</td><td colspan="3">Filt. Mg, K, Na, Li, NH_4.
Add $(NH_4)_2HPO_4$, agitate and filter.</td></tr>
<tr><td colspan="2">Ppt. Co, Ni.
Wash, dissolve in HCl, evaporate almost to dryness, add H_2O, and treat with KCN and HCl, according to chart on page 834, add KOH until alkaline, and filter.</td><td rowspan="2">Filt. Zn.
Add NH_4HS, warm, allow to stand. White ppt.</td><td rowspan="2">Ppt. Ba.
Yellow.</td><td colspan="2">Filt. Sr, Ca.
Add very dilute H_2SO_4, allow to stand for 10 minutes, filter.</td><td rowspan="2">Ppt. Mg.
White, crystalline.</td><td colspan="2">Filt. K, Na, Li, NH_4.
Add Na_2HPO_4 and NaOH, boil until all NH_3 is expelled, and filter.</td></tr>
<tr><td>Ppt. Ni.
Green. Wash well, allow to drain, and test with borax bead. Reddish-brown color.</td><td>Filtrate Co.
Evaporate to dryness, and test residue with borax bead. Blue color.</td><td>Ppt. Sr.
White. Confirm by flame test. Intense red color.</td><td>Filt. Ca.
Add NH_4OH in excess and $(NH_4)_2C_2O_4$. White ppt.</td><td>Ppt. Li.
White. Confirm by flame test. Crimson color.</td><td>Filt. K, Na.
Acidify with $HC_2H_3O_2$, add $Co_2(NO_2)_6$-$6NaNO_2$. Yellow ppt. indicates K.
Test original solution for Na and NH_4.</td></tr>
</table>

* See Note 1 on following page.

† See Note 2 on following page.

NOTES ON THE PRECEDING CHART.

1. It is particularly important not to filter immediately after adding NH_4HS in the first precipitation, otherwise the Mn will not be thoroughly precipitated.

2. When Ni is present it may remain in solution in the NH_4HS, causing the filtrate to be dark; in which case a dark precipitate of NiS will separate upon evaporating the filtrate in a dish to remove NH_4HS.

The indication of the complete removal of the NH_4HS is a colorless, supernatant liquid, either remaining from the partial evaporation of the filtrate, or obtained by adding H_2O to the residue in the case of evaporation to dryness.

After filtering proceed with the colorless filtrate, while the NiS on the filter is being washed and afterwards dissolved along with the precipitate of Mn, Zn, Co, Ni, and in the same boiling-hot mixture of HCl and HNO_3.

Group IV. Iron, Cerium, Aluminum, Chromium.

REACTIONS OF IRON AS SOLUBLE FERROUS SALTS.

Use a 2-per-cent. solution of ferrous sulphate, $FeSO_4.7H_2O$.

1. $K_4Fe(CN)_6$, in neutral or slightly acid solution, gives a white (rapidly changing to light blue) precipitate of **potassium ferrous ferrocyanide**, $K_2Fe(Fe(CN)_6)$, known as Everett's salt.

$$FeSO_4 + K_4Fe(CN)_6 = K_2Fe(Fe(CN)_6) + K_2SO_4.$$

Alkali hydrates decompose this compound, forming **ferrous hydrate**, $Fe(OH)_2$, and a ferrocyanide of the base used.

$$K_2Fe(Fe(CN)_6) + 2KOH = Fe(OH)_2 + K_4Fe(CN)_6.$$

2. $K_6Fe_2(CN)_{12}$, in neutral or slightly acid solution, forms a dark-blue precipitate of **ferrous ferricyanide**, $Fe_3Fe_2(CN)_{12}$, known as Turnbull's blue.

$$3FeSO_4 + K_6Fe_2(CN)_{12} = Fe_3Fe_2(CN)_{12} + 3K_2SO_4.$$

If the solutions be very dilute there is produced merely a deep blue-green coloration. Alkali hydrates decompose the precipitate.

3. KCNS produces no change in color.

4. H_2S, in acid solution, does not cause a precipitate.

5. NH_4HS, with a neutral or alkaline solution, forms a black precipitate of **ferrous sulphide**, FeS, soluble in HCl or HNO_3. NH_4Cl promotes the formation of this precipitate.

6. KOH or NaOH, or NH_4OH in the absence of NH_4Cl, produces a dirty-green precipitate of **ferrous hydrate**, $Fe(OH)_2$.

8. With borax in the oxidizing blowpipe flame ferrous and ferric compounds give **dark yellow-colored** beads while hot, and **paler yellow** when cold. In the reducing flame the beads change to **bottle-green.**

REACTIONS OF SOLUBLE SALTS OF CERIUM.

Use a 2-per-cent. solution of cerous chloride, Ce_2Cl_6.

1. NH_4HS causes a white precipitate of **cerous hydrate,** $Ce_2(OH)_6$, H_2S being liberated.

$$Ce_2Cl_6 + 6NH_4HS + 6H_2O = Ce_2(OH)_6 + 6NH_4Cl + 6H_2S.$$

2. KOH, NaOH, or NH_4OH produces the same precipitate of $Ce_2(OH)_6$.

3. $(NH_4)_2C_2O_4$ forms a white precipitate of **cerous oxalate,** $Ce_2(C_2O_4)_3$.

4. Na_2HPO_4 precipitates white **cerous phosphate,** $Ce_2(PO_4)_2$.

$$Ce_2Cl_6 + 2Na_2HPO_4 = Ce_2(PO_4)_2 + 4NaCl + 2HCl.$$

Organic matter does not interfere with the formation of this precipitate.

5. With a borax bead before the blowpipe the salts of cerium behave like those of iron.

REACTIONS OF SOLUBLE SALTS OF ALUMINUM.

Use a 2-per-cent. solution of potassium alum, $Al_2K_2(SO_4)_4 \cdot 24H_2O$.

1. NH_4HS produces a white gelatinous precipitate of **aluminum hydrate,** $Al_2(OH)_6$, H_2S being set free.

2. NH_4OH precipitates $Al_2(OH)_6$, which is insoluble in excess of the reagent (an important distinction from zinc). Heat facilitates this precipitation.

3. KOH or NaOH causes a precipitate of $Al_2(OH)_6$, which dissolves in an excess to form an **aluminate** of the base used, as, for instance, $Al_2(OK)_6$. This is not reprecipitated by boiling (a distinction from zinc and chromium); but, when warmed with NH_4Cl, decomposition ensues with precipitation of $Al_2(OH)_6$.

$$Al_2(OK)_6 + 6NH_4Cl = Al_2(OH)_6 + 6NH_3 + 6KCl.$$

4. K_2CO_3 or Na_2CO_3 produces $Al_2(OH)_6$, insoluble in excess, CO_2 escaping at the same time.

The presence of non-volatile organic acids and sugar prevents the complete precipitation in the foregoing reactions.

REACTIONS OF SOLUBLE SALTS OF CHROMIUM.

Use a 2-per-cent. solution of chromic chloride, Cr_2Cl_6.

1. NH_4HS produces a greenish precipitate of **chromic hydrate**, $Cr_2(OH)_6$, H_2S being set free.

2. NH_4OH forms the same precipitate of $Cr_2(OH)_6$, insoluble in excess of the reagent.

3. KOH or NaOH causes the precipitation of $Cr_2(OH)_6$, which is soluble in an excess, but reprecipitated on boiling (a distinction from aluminum).

4. K_2CO_3 or Na_2CO_3 precipitates green **basic chromium carbonate.**

5. When a salt of chromium is fused on a platinum foil with a mixture of 1 part KNO_3 and 2 parts K_2CO_3, the mass becomes yellow from the formation of **potassium chromate,** K_2CrO_4.

$$Cr_2Cl_6 + 2KNO_3 + 4K_2CO_3 = 2K_2CrO_4 + N_2O_2 + 6KCl + 4CO_2.$$

The presence of this compound may be proved by dissolving the cooled mass in water, and, after acidifying with acetic acid, adding $AgNO_3$ or $Pb(C_2H_3O_2)_2$, the former of which precipitates red **silver chromate,** Ag_2CrO_4, and the latter yellow **lead chromate,** $PbCrO_4$, if K_2CrO_4 be present.

$$K_2CrO_4 + Pb(C_2H_3O_2)_2 = PbCrO_4 + 2KC_2H_3O_2.$$

If sodium salts be substituted, Na_2CrO_4 will be obtained.

6. With the borax bead in the inner blowpipe flame chromium compounds give a **green** color.

CHART FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP IV.

<table>
<tr><td colspan="4">Evaporate a portion of the original solution to dryness, mix the residue intimately with 2 parts Na_2CO_3 and 1 part KNO_3, and fuse on platinum foil. Boil the cooled mass in a dish with a bulk of water equal to that of the solution evaporated, allow to subside, and decant the liquid upon a filter.</td></tr>
<tr><td colspan="2">Precipitate Fe, Ce.
Wash by decantation, dissolve by heating in the dish with 5 drops H_2SO_4 and 20 drops C_2H_5OH, dilute with water, filter, and divide into two portions.</td><td colspan="2">Filtrate Al, Cr.
Yellow, if Cr be present. Divide into two portions.</td></tr>
<tr><td>Fe.
Add $K_4Fe(CN)_6$. Blue ppt. Test original solution with $K_4Fe(CN)_6$ and $K_6Fe_2(CN)_{12}$ for Fe(ic) and Fe(ous).</td><td>Ce.
Add $H_3C_6H_5O_7$, NH_4OH in excess, and Na_2HPO_4. White ppt.</td><td>Al.
Add NH_4Cl, warm, and allow to stand. White, gelatinous ppt.</td><td>Cr.
Acidify with $HC_2H_3O_2$ and add $Pb(C_2H_3O_2)_2$. Yellow ppt.</td></tr>
</table>

CHART FOR THE DETECTION OF BASES IN SOLUTIONS CONTAINING SOLUBLE SALTS OF ALL FOREGOING ELEMENTS.

Fe, Ce, Al, Cr, Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH_4.
Add to the original solution NH_4Cl, NH_4OH, NH_4HS, warm well and filter.

- **Precipitate Fe, Ce, Al, Cr, Mn, Zn, Co, Ni.** Wash, dissolve in a boiling-hot mixture of 2 parts HCl and 1 part HNO_3, evaporate almost to dryness, add H_2O and then NH_4OH in excess, agitate and filter.
  - **Ppt. Fe, Ce, Al, Cr.** Wash, allow to drain, mix with 2 parts Na_2CO_3 and 1 part KNO_3, fuse on platinum foil, allow to cool, boil with H_2O, and decant the liquid upon a filter.
    - **Ppt. Fe, Ce.** Wash by decantation, dissolve by heating in the dish with 5 drops H_2SO_4 and 20 drops C_2H_5OH, dilute with H_2O, filter, and divide into two portions.
      - **Fe.** Add $K_4Fe(CN)_6$. Blue ppt. Test original solution for Fe(ous) and Fe(ic).
      - **Ce.** Add $H_3C_6H_5O_7$, NH_4OH in excess, and Na_2HPO_4. White ppt.
    - **Filt. Al, Cr.** Yellow, if Cr be present. Divide into two portions.
      - **Al.** Add NH_4Cl, warm well, and allow to stand. White, gelatinous ppt.
      - **Cr.** Acidify with $HC_2H_3O_2$, and add $Pb(\bar{A})_2$. Yellow ppt.
  - **Filt. Mn, Zn, Co, Ni.** Acidify slightly with $HC_2H_3O_2$, warm, add H_2S, and filter.
    - **Ppt. Zn, Co, Ni.** Wash, dissolve in boiling-hot HCl and HNO_3, evaporate almost to dryness, add H_2O and then KOH until alkaline, agitate, and filter.
      - **Ppt. Co, Ni.** Wash, dissolve in hot HCl. Evaporate almost to dryness, add H_2O, and treat with KCN and HCl, according to chart, page 834, add KOH until alkaline, filter.
        - **Ppt. Ni.** Green. Confirm by borax bead.
        - **Filt. Co.** Evaporate to dryness and test with borax bead.
      - **Filt. Zn.** Add NH_4HS, warm, allow to stand. White ppt.
    - **Filt. Mn.** Add NH_4OH until alkaline and H_2S. Flesh-colored ppt. Apply Crum's test to original solution.
- **Filtrate Ba, Sr, Ca, Mg, K, Na, Li, NH_4.** (If Ni is suspected proceed by note on page 830.) Evaporate to remove NH_4HS, add $(NH_4)_2CO_3$, boil, filter.
  - **Ppt. Ba, Sr, Ca.** Wash, dissolve in $HC_2H_3O_2$, dilute, add K_2CrO_4, and filter.
    - **Ppt. Ba.** Yellow.
    - **Filt. Sr, Ca.** Add very dilute H_2SO_4, allow to stand for 10 minutes, filter.
      - **Ppt. Sr.** White. Confirm by flame test.
      - **Filt. Ca.** Add NH_4OH in excess and $(NH_4)_2C_2O_4$. White ppt.
  - **Filt. Mg, K, Na, Li, NH_4.** Add $(NH_4)_2HPO_4$, agitate, and filter.
    - **Ppt. Mg.** White, crystalline.
    - **Filt. K, Na, Li, NH_4.** Add Na_2HPO_4 and NaOH, boil until all NH_3 is expelled, and filter.
      - **Ppt. Li.** White. Confirm by flame test.
      - **Filt. K, Na.** Acidify with $HC_2H_3O_2$, add $Co_2(NO_2)_6 6NaNO_2$. Yellow ppt. indicates K.
        - Test original solution for Na and NH_4.

NOTES ON THE PRECEDING CHART.

1. When the first precipitate is dissolved in HCl and HNO_3, the Fe must be completely oxidized by boiling with the HNO_3, that the precipitation as $Fe_2(OH)_6$ by the NH_4OH shall be complete.

2. When phosphoric acid is present the members of Group II. precipitate with Group IV., and require an entirely different method of separation. It is desirable, however, for the student first to familiarize himself with these simpler soluble salts, and undertake the more difficult cases of salts insoluble in water only after the acids have been considered. (See page 878.)

Group V. Arsenic, Antimony, Tin, Gold, Platinum.

REACTIONS OF SOLUBLE ARSENOUS COMPOUNDS.

Use a 1-per-cent. solution of arsenous oxide, As_2O_3.

1. H_2S produces a yellow color, but no precipitate, until HCl is added, when a yellow precipitate of **arsenous sulphide,** As_2S_3, falls.

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O.$$

This precipitate is insoluble in boiling HCl, but soluble in NH_4HS, $(NH_4)_2S$, NH_4OH, or $(NH_4)_2CO_3$, from which it is reprecipitated by acidifying with HCl.

2. NH_4HS causes the formation of As_2S_3, which remains in solution as **ammonium sulpharsenite,** $(NH_4)_3AsS_3$.

$$As_2O_3 + 6NH_4HS = 2(NH_4)_3AsS_3 + 3H_2O.$$

On the addition of HCl, As_2S_3 is precipitated.

$$2(NH_4)_3AsS_3 + 6HCl = As_2S_3 + 6NH_4Cl + 3H_2S.$$

3. $AgNO_3$ produces no precipitate until a few drops of dilute NH_4OH are added, when a yellow precipitate of **silver arsenite,** Ag_3AsO_3, falls.

$$As_2O_3 + 6AgNO_3 + 6NH_4OH = 2Ag_3AsO_3 + 6NH_4NO_3 + 3H_2O.$$

The precipitate is soluble in an excess of NH_4OH, and in HNO_3.

4. $CuSO_4$, under similar circumstances, produces a yellowish-green precipitate of **cupric arsenite,** $CuHAsO_3$.

$$As_2O_3 + 2CuSO_4 + 4NH_4OH = 2CuHAsO_3 + 2(NH_4)_2SO_4 + H_2O.$$

REACTIONS OF SOLUBLE ARSENIC COMPOUNDS.

Use a 1-per-cent. solution of sodium arsenate, $Na_2HAsO_4.7H_2O$.

1. H_2S causes, in acid solution only, a yellow precipitate of **arsenous sulphide,** As_2S_3, mixed with sulphur.

$$2Na_2HAsO_4 + 5H_2S + 4HCl = As_2S_3 + S_2 + 4NaCl + 8H_2O$$

This reaction takes place slowly, but is accelerated by heat.

2. NH_4HS produces no precipitate, but forms **arsenic sulphide,** As_2S_5, which remains in solution as **ammonium sulpharsenate,** $(NH_4)_3AsS_4$.

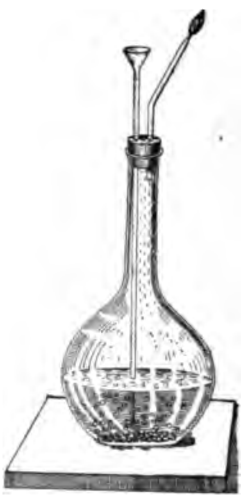
$$Na_2HAsO_4 + 5NH_4HS = (NH_4)_3AsS_4 + Na_2S + 2NH_3 + 4H_2O.$$

Upon the addition of HCl, As_2S_5 is precipitated, and no As_2S_3 and S.

$$2(NH_4)_3AsS_4 + 6HCl = As_2S_5 + 6NH_4Cl + 3H_2S.$$

3. $AgNO_3$ with a small amount of NH_4OH produces a chocolate-colored precipitate of **silver arsenate,** Ag_3AsO_4, soluble in excess of NH_4OH and in HNO_3.

FIG. 110.



Marsh's test.

4. $CuSO_4$, under similar circumstances, forms a bluish-green precipitate of **cupric arsenate,** $CuHAsO_4$.

The following tests are applicable to both arsenous and arsenic compounds :

1. **Marsh's Test.**—Generate hydrogen in the usual way, allowing it to escape through a glass tube drawn out at the end so as to form a small orifice (Fig. 110).

In very exact cases, the gas should be dried by passing over anhydrous calcium chloride. When all the air has been expelled (which should be determined by collecting a small test-tube full and holding its mouth to a flame; if the gas burn quietly, without explosion, it is pure), ignite the escaping gas. It should burn with a colorless or yellow flame,—in the latter case the color is due to the sodium in the glass. To make sure that the zinc and sulphuric gently, when a white ring of **arsenous oxide,** As_2O_3, will form on the tube above the copper, and is readily distinguished by the characteristic octohedral shape of the crystals composing it.

$$Cu_5As_2 + 4O_2 \text{ (from the air)} = As_2O_3 + 5CuO.$$

The CuO is not volatile.

4. **Fleitmann's Test.**—Generate hydrogen in a test-tube from zinc and solution of potassium hydrate; moisten a piece of filter paper with one drop of solution of silver nitrate, place it over the mouth of the tube and heat the mixture,—there should be no coloration of the moistened spot on the paper if the reagents are free from arsenic. Now add some soluble compound of arsenic, and the silver nitrate will immediately become black, owing to the liberation of metallic **silver,** Ag.

$$H_3As + 6AgNO_3 + 3H_2O = 3(Ag_2) + H_3AsO_3 + 6HNO_3.$$

Gatehouse's modification of this test consists in employing aluminum wire cut into small pieces instead of zinc. The method of application and results are the same.

5. **Bettendorff's Test.**—To some boiling hydrochloric acid add granulated tin or tin-foil until no more is dissolved. Pour off the liquid and mix it with an equal volume of hydrochloric acid. Boil again; if no coloration or precipitate forms the materials are free from arsenic. Should this be the case, add a relatively small quantity of a solution containing a compound of arsenic and continue to heat. A brown color or precipitate of metallic **arsenic,** As, with a small amount of tin results.

$$As_2O_3 + 6HCl + 3SnCl_2 = As_2 + 3SnCl_4 + 3H_2O.$$

6. Before the blowpipe, on charcoal, arsenic is volatilized, with the characteristic odor of garlic.

REACTIONS OF SOLUBLE ANTIMONY COMPOUNDS.

Use a 1-per-cent. solution of tartar emetic, $2K(SbO)C_4H_4O_6 \cdot H_2O$.

1. H_2S forms, in solutions acidified with HCl, an orange-colored precipitate of **antimonous sulphide,** Sb_2S_3, soluble in NH_4HS, $(NH_4)_2S$, or boiling HCl, but insoluble in $(NH_4)_2CO_3$.

2. NH_4HS produces a precipitate of Sb_2S_3, readily soluble in excess with the formation of **ammonium sulphantimonite,** $(NH_4)_3SbS_3$, from which HCl again precipitates Sb_2S_3.

3. KOH or NaOH precipitates white **antimonous hydrate,** $Sb(OH)_3$, soluble in an excess of the reagent.

4. NH_4OH precipitates $Sb(OH)_3$, insoluble in an excess of the reagent.

5. Marsh's Test, applied as with arsenic, gives a sooty-black spot of metallic **antimony,** Sb, which is insoluble in NaOCl or $Ca(OCl)_2$, but soluble in NH_4HS.

6. Gutzeit's Test gives at once a black or brown stain of **silver antimonide,** Ag_3Sb.

$$3AgNO_3 + H_3Sb = Ag_3Sb + 3HNO_3.$$

7. Reinsch's Test causes a deposit of Sb on the copper, as with arsenic, but when heated in a tube there is formed a white, amorphous ring of **antimonous oxide,** Sb_2O_3, which is readily distinguished from the crystalline one obtained in the reaction of arsenic.

8. Fleitmann's Test gives no result with antimony compounds, because **hydrogen antimonide,** H_3Sb, is decomposed by alkali hydrates.

9. Bettendorff's Test shows no reaction with antimony, as $SnCl_2$ does not precipitate Sb.

10. Zn and Pt (foil), when warmed with a solution of an antimony compound acidified with HCl, cause a deposition of finely-divided, black metallic Sb upon the Pt, H_3Sb being at the same time evolved.

$$3SbCl_3 + 6H_2 = Sb_2 + 9HCl + H_3Sb.$$

If the foil be warmed in a dish with a few drops of dilute HNO_3, the black Sb will be converted into white Sb_2O_3, soluble in $H_2C_4H_4O_6$.

$$Sb_2 + 2HNO_3 = Sb_2O_3 + H_2O + N_2O_2.$$

11. On charcoal, with Na_2CO_3, before the blowpipe, antimony compounds yield a metallic globule of Sb, while characteristic fumes of white Sb_2O_3 are given off.

REACTIONS OF TIN AS SOLUBLE STANNOUS SALTS.

Use a 2-per-cent. solution of stannous chloride, $SnCl_2.2H_2O$.

1. H_2S precipitates dark-brown **stannous sulphide,** SnS, soluble in boiling HCl or in $(NH_4)_2S$, but insoluble in NH_4HS.

2. KOH or NaOH precipitates white **stannous hydrate,** $Sn(OH)_2$, soluble in an excess of the reagent. On boiling this solution **stannous oxide,** SnO, is precipitated.

$$Sn(OK)_2 + H_2O = SnO + 2KOH.$$

3. NH_4OH precipitates $Sn(OH)_2$, insoluble in an excess of th reagent.

4. $HgCl_2$ causes a white precipitate of **mercurous chloride** Hg_2Cl_2, the $SnCl_2$ being converted into $SnCl_4$.

$$SnCl_2 + 2HgCl_2 = Hg_2Cl_2 + SnCl_4.$$

This precipitate is blackened by the addition of NH_4OH.

REACTIONS OF TIN AS SOLUBLE STANNIC SALTS.

Use a 2-per-cent. solution of stannic chloride, $SnCl_4.5H_2O$.

1. H_2S produces a yellow precipitate of **stannic sulphide** SnS_2, soluble in boiling HCl, NH_4HS, or $(NH_4)_2S$.

2. KOH or NaOH precipitates white **stannic acid,** H_2SnO_3

$$SnCl_4 + 4KOH = H_2SnO_3 + 4KCl + H_2O.$$

The precipitate is soluble in an excess of the reagent; on boiling, no precipitation takes place (distinction from stannous salts)

$$H_2SnO_3 + 2KOH = K_2SnO_3 + 2H_2O.$$

3. NH_4OH produces a precipitate of H_2SnO_3, insoluble in a excess of the reagent.

4. Heated on charcoal, before the blowpipe, with Na_2CO_3 an KCN, metallic **tin**, Sn, is formed from both Sn(ous) and Sn(ic compounds, with the production of a white incrustation of **stannic oxide,** SnO_2.

5. Zn and Pt (foil), warmed with a solution of a salt of ti acidified with HCl, effects the separation of the Sn as a soft metallic sediment, soluble in hot HCl.

$$2SnCl_2 + 2H_2 = Sn_2 + 4HCl.$$

REACTIONS OF SOLUBLE SALTS OF GOLD.

Use a 0.5-per-cent. solution of auric chloride, $AuCl_3$.

1. H_2S precipitates black **auric sulphide,** Au_2S_3, insoluble i boiling HCl, NH_4HS, or $(NH_4)_2CO_3$, but soluble in $(NH_4)_2S$ o a mixture of HCl and HNO_3.

2. $H_2C_2O_4$ or $FeSO_4$ precipitates **metallic gold,** Au, as a finely-divided brown powder.

$$2AuCl_3 + 3H_2C_2O_4 = Au_2 + 6HCl + 6CO_2.$$
$$2AuCl_3 + 6FeSO_4 + 3H_2SO_4 = Au_2 + 3Fe_23SO_4 + 6HCl.$$

3. $SnCl_2$ mixed with $SnCl_4$ and $FeCl_2$ (prepared by adding Fe_2Cl_6 to $SnCl_2$) produces a purple-red precipitate or coloration

(Purple of Cassius), consisting of the **mixed oxides of gold and tin.**

4. Heated on charcoal, before the blowpipe, salts of gold yield metallic Au.

REACTIONS OF SOLUBLE SALTS OF PLATINUM.

Use a 2-per-cent. solution of platinic chloride, $PtCl_4.5H_2O$.*

1. H_2S causes a brown precipitate of **platinic sulphide,** PtS_2, insoluble in boiling HCl, NH_4HS, or $(NH_4)_2CO_3$, but soluble in $(NH_4)_2S$ or a mixture of HCl and HNO_3.

2. KCl produces a yellow, crystalline precipitate of **potassium platinic chloride,** K_2PtCl_6. The presence of alcohol facilitates the precipitation in this and the next test.

3. NH_4Cl forms a similar precipitate of **ammonium platinic chloride,** $(NH_4)_2PtCl_6$.

4. Fe or Zn precipitates finely-divided black metallic **platinum,** Pt.

5. Heated on charcoal, before the blowpipe, compounds of platinum yield metallic Pt.

CHART FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP V.

<table>
<tr><td colspan="4">Acidify the original solution with HCl, warm, and add H_2S. Filter (disregard the filtrate after making sure that the precipitation has been complete), transfer the precipitate to a dish, boil with strong HCl, and filter.</td></tr>
<tr><td colspan="3">Precipitate As, Au, Pt.
If yellow, As only is present; if dark, wash, digest with $(NH_4)_2CO_3$, and filter.</td><td rowspan="3">Filtrate Sb, Sn.
Dilute with H_2O, boil in a dish with a piece of platinum foil and a small fragment of zinc, so the metals touch. The platinum will be coated with black, metallic Sb, while the Sn will be deposited as a metallic sediment. This sediment is dissolved in HCl and tested with $HgCl_2$, which produces a white precipitate if Sn be present. Warm the foil with a few drops of HNO_3 in a dish until the black color disappears, rinse with solution of $H_2C_4H_4O_6$, pour into a test-tube and add H_2S; orange-colored precipitate if Sb be present.</td></tr>
<tr><td colspan="2">Precipitate Au, Pt.
Dissolve in 2 parts HCl and 1 part HNO_3. Divide into two portions.</td><td rowspan="2">Filt. As.
Acidify with HCl. Yellow ppt.</td></tr>
<tr><td>Au.
Apply Purple of Cassius test to this and also to original solution.</td><td>Pt.
Add KCl. Yellow ppt. Confirm by testing original solution.</td></tr>
</table>

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* Or chloroplatinic acid, $H_2PtCl_6.6H_2O$.

NOTES ON THE PRECEDING CHART.

1. In the application of H_2S the solution to be tested should always be well warmed and very thoroughly saturated with the reagent, otherwise the precipitation of As, when present in the arsenic state, will not be complete.

2. To transfer a precipitate to a dish use is made of the wash-bottle, the jet from which is directed against the moist precipitate on the unfolded filter in such a way that the least possible quantity of water may be used. After settling, the greater part of the water should be decanted from the precipitate, which should then be treated with the next reagent.

3. If stannic salts are known to be absent, and the precipitate produced by H_2S is yellow, As only is present; if orange-colored, Sb is present, and As may be. Under such circumstances, the readiest method of separation is to wash the precipitate and then treat it with $(NH_4)_2CO_3$; As will be dissolved, and may be detected in the filtrate by acidifying with HCl, while Sb remains on the filter.

ELEMENTS.

<table>
<tr><td colspan="15">As, Sb, Sn, Au, Pt, Fe, Ce, Al, Cr, Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH_4.
Acidify the original solution with HCl, then add H_2S until, after warming, the mixture smells strongly of the reagent, and filter.</td></tr>
<tr><td colspan="2" rowspan="2">Ppt. As, Sb, Sn, Au, Pt.
Wash, boil with strong HCl, and filter.</td><td colspan="13">Filt. Fe, Ce, Al, Cr, Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH_4.
Add NH_4Cl, NH_4OH, NH_4HS, warm well, and filter.</td></tr>
<tr><td colspan="7">Ppt. Fe, Ce, Al, Cr, Mn, Zn, Co, Ni.
Wash, dissolve in 2 parts HCl and 1 part HNO_3, evaporate almost to dryness, add H_2O and then NH_4OH in excess, and filter.</td><td colspan="6">Filt. Ba, Sr, Ca, Mg, K, Na, Li, NH_4.
Evaporate to remove NH_4HS, add $(NH_4)_2CO_3$, boil, filter.</td></tr>
<tr><td rowspan="4">Ppt. As, Au, Pt.
Separate according to chart, p. 847.</td><td rowspan="4">Filt. Sb, Sn.
Separate according to chart, p. 847.</td><td colspan="3">Ppt. Fe, Ce, Al, Cr.
Wash, allow to drain, fuse on foil with Na_2CO_3 and KNO_3, boil cooled mass with H_2O, decant upon a filter.</td><td colspan="4">Filt. Mn, Zn, Co, Ni.
Acidify slightly with $HC_2H_3O_2$, add H_2S, filter.</td><td colspan="3">Ppt. Ba, Sr, Ca.
Wash, dissolve in $HC_2H_3O_2$, dilute, add K_2CrO_4, filter.</td><td colspan="3">Filt. Mg, K, Na, Li, NH_4.
Add $(NH_4)_2HPO_4$, agitate, filter.</td></tr>
<tr><td rowspan="3">Ppt. Fe, Ce.
Separate according to chart, p. 839.</td><td colspan="2">Filt. Al, Cr.
Yellow, if Cr be present. Divide into two portions.</td><td colspan="3">Ppt. Zn, Co, Ni.
Wash, dissolve in 2 parts HCl and 1 part HNO_3, evaporate almost to dryness, add H_2O and then KOH until distinctly alkaline, filter.</td><td rowspan="3">Filt. Mn.
Add NH_4OH in excess and H_2S. Flesh-colored ppt. Apply Crum's test to original solution.</td><td rowspan="3">Ppt. Ba.
Yellow.</td><td colspan="2">Filt. Sr, Ca.
Add very dilute H_2SO_4, allow to stand, filter.</td><td rowspan="3">Ppt. Mg.
White, crystalline.</td><td colspan="2">Filt. K, Na, Li, NH_4.
Add Na_2HPO_4 and NaOH, boil until all NH_3 is expelled, and filter.</td></tr>
<tr><td rowspan="2">Al.
Add NH_4Cl, warm well, and allow to stand. White, gelatinous ppt.</td><td rowspan="2">Cr.
Acidify with $HC_2H_3O_2$ and add $Pb(A)_2$. Yellow ppt.</td><td colspan="2">Ppt. Co, Ni.
Wash, dissolve in HCl, evaporate almost to dryness, add H_2O, and treat with KCN and HCl according to chart, p. 834, then add KOH until alkaline, filter.</td><td rowspan="2">Filt. Zn.
Add NH_4HS, warm, allow to stand. White ppt.</td><td rowspan="2">Ppt. Sr.
White. Confirm by flame test.</td><td rowspan="2">Filt. Ca.
Add NH_4OH in excess and $(NH_4)_2C_2O_4$. White ppt.</td><td rowspan="2">Ppt. Li.
White. Confirm by flame test.</td><td>Filt. K, Na.
Acidify with $HC_2H_3O_2$, add $Co_2(NO_2)_6$-$6NaNO_2$. Yellow ppt. indicates K.</td></tr>
<tr><td>Ppt. Ni.
Green. Confirm by borax bead.</td><td>Filt. Co.
Evaporate to dryness and test with borax bead.</td><td>Test original solution for Na and NH_4.</td></tr>
</table>

Group VI. Mercury(ic), Bismuth, Copper, Cadmium.

REACTIONS OF SOLUBLE MERCURIC SALTS.

Use a 2-per-cent. solution of mercuric chloride, $HgCl_2$.

1. H_2S or NH_4HS produces, when in small proportion, a whitish precipitate of $(HgS)_2HgCl_2$; a further addition of the reagent, together with the application of heat, causes the formation of a black precipitate of **mercuric sulphide,** HgS, insoluble in either HCl or HNO_3, but soluble in a mixture of the two. It is insoluble also in NH_4HS or $(NH_4)_2S$.

2. KOH or NaOH produces a yellow precipitate of **mercuric oxide,** HgO.

$$HgCl_2 + 2KOH = HgO + 2KCl + H_2O.$$

Unless the reagent be in excess a brown precipitate of a basic salt is formed.

3. NH_4OH precipitates white **mercuric ammonium chloride,** NH_2HgCl.

$$HgCl_2 + 2NH_4OH = NH_2HgCl + NH_4Cl + 2H_2O.$$

This precipitate is readily soluble in HCl or $HC_2H_3O_2$.

4. K_2CrO_4 produces a red precipitate of **mercuric chromate,** $HgCrO_4$.

5. KI precipitates **mercuric iodide,** HgI_2, at first yellow, but rapidly becoming scarlet.

$$HgCl_2 + 2KI = HgI_2 + 2KCl.$$

This precipitate is readily soluble in excess of KI or $HgCl_2$.

6. $SnCl_2$, in small quantity, in the presence of HCl, precipitates white **mercurous chloride,** Hg_2Cl_2. On the addition of a larger quantity of the reagent, Hg_2Cl_2 is reduced to gray metallic **mercury,** Hg, which may be collected into a globule.

$$Hg_2Cl_2 + SnCl_2 = Hg_2 + SnCl_4.$$

7. Na_2CO_3 produces a reddish-brown precipitate of **basic mercuric carbonate,** $HgCO_3(HgO)_3$.

8. Copper turnings boiled with the solution, acidified with HCl, become quickly coated with metallic **mercury,** Hg.

$$2HgCl_2 + Cu_2 = Hg_2 + 2CuCl_2.$$

The presence of HNO_3 must be avoided or the copper will be dissolved; when present in the material to be tested, it should be expelled by evaporating the solution with HCl to dryness. If the coated turnings are carefully dried at a low temperature, placed in the bottom of a dry, narrow test-tube and heated, a ring composed of minute globules of Hg will form on the cool part of the tube. These globules may be formed into larger ones by pressing them together with a glass rod, until they may be seen with the naked eye.

9. Before the blowpipe, HgO breaks up into Hg and O. HgS, under similar circumstances, sublimes unchanged.

Reactions of Soluble Salts of Bismuth.

Use a 2-per-cent. solution of bismuth nitrate, $Bi(NO_3)_3.5H_2O$.

1. H_2S or NH_4HS produces a black precipitate of **bismuth trisulphide,** Bi_2S_3, insoluble in NH_4HS or $(NH_4)_2S$, but soluble in boiling HNO_3.

2. KOH, NaOH, or NH_4OH forms a white precipitate of **bismuth hydrate,** $Bi(OH)_3$, converted, through loss of H_2O by boiling, into yellow **bismuth oxide,** Bi_2O_3.

$$2Bi(OH)_3 = Bi_2O_3 + 3H_2O.$$

Both compounds dissolve in HCl to form **bismuth chloride,** $BiCl_3$.

3. K_2CrO_4 precipitates yellow **bismuth chromate,** $Bi_2(CrO_4)_3$.

4. KI forms a brown precipitate of **bismuth iodide,** BiI_3, soluble in excess of the reagent.

5. H_2O in considerable quantity, when there is not an excess of free acid, precipitates white **bismuth subnitrate,** $BiONO_3.H_2O$.

$$Bi(NO_3)_3 + 2H_2O = BiONO_3.H_2O + 2HNO_3.$$

When bismuth chloride is so diluted, white **bismuth oxychloride,** BiOCl, is produced.

6. Na_2CO_3 precipitates white **bismuth subcarbonate,** $(BiO)_2CO_3.H_2O$.

$$2Bi(NO_3)_3 + 3Na_2CO_3 + H_2O = (BiO)_2CO_3.H_2O + 6NaNO_3 + 2CO_2.$$

7. Bismuth salts on charcoal, before the blowpipe, yield a hard bead of **bismuth,** Bi, and a characteristic incrustation of **bismuth oxide,** Bi_2O_3, deep orange-yellow while hot, but pale yellow when cold.

REACTIONS OF SOLUBLE SALTS OF COPPER.

Use a 2-per-cent. solution of cupric sulphate, $CuSO_4.5H_2O$.

1. H_2S or NH_4HS precipitates black **cupric sulphide**, CuS, slightly soluble in $(NH_4)_2S$ and NH_4HS, but readily dissolved by KCN or boiling HNO_3.

2. KOH or NaOH produces a light-blue precipitate of **cupric hydrate**, $Cu(OH)_2$, insoluble in excess of the reagent.

In the presence of non-volatile organic acids this precipitation does not take place, but a blue color results.

Boiling converts the $Cu(OH)_2$, through loss of H_2O, into black **cupric oxyhydrate**, $(CuO)_2Cu(OH)_2$.

$$3Cu(OH)_2 = (CuO)_2Cu(OH)_2 + 2H_2O.$$

3. NH_4OH in small quantity forms a greenish-purple precipitate, readily soluble in an excess of the reagent, forming **tetra-ammonio-cupric sulphate**, $(NH_3)_4CuSO_4.H_2O$, which imparts to the solution an azure-blue color.

$$CuSO_4 + 4NH_4OH = (NH_3)_4CuSO_4.H_2O + 3H_2O.$$

4. $K_4Fe(CN)_6$ precipitates reddish-brown **cupric ferrocyanide**, $Cu_2Fe(CN)_6$.

5. Metallic Fe or Zn precipitates red metallic **copper**, *Cu*, which collects on the Fe or Zn.

6. In the outer blowpipe flame copper salts color the borax bead **green** while hot, and **blue** when cold. In the inner flame, after moistening with $SnCl_2$, the bead becomes **red**, owing to the formation of **cuprous oxide**, Cu_2O.

REACTIONS OF SOLUBLE SALTS OF CADMIUM.

Use a 2-per-cent. solution of cadmium nitrate, $Cd(NO_3)_2.4H_2O$.

1. H_2S or NH_4HS precipitates yellow **cadmium sulphide**, CdS, insoluble in $(NH_4)_2S$, NH_4HS, or KCN, but soluble in hot HNO_3 or dilute H_2SO_4.

2. KOH or NaOH produces a white precipitate of **cadmium hydrate**, $Cd(OH)_2$, insoluble in excess of the reagent.

3. NH_4OH causes the precipitation of $Cd(OH)_2$, which dissolves in an excess of the reagent.

4. Na_2CO_3 produces a white precipitate of **cadmium oxycarbonate**, insoluble in excess, but slightly soluble in ammonium salts, and readily soluble in NH_4OH.

5. On charcoal, before the blowpipe, the salts of cadmium are

reduced to **cadmium**, Cd, and volatilize, forming a brownish incrustation of **cadmium oxide**, CdO.

CHART FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP VI.

<table>
<tr><td colspan="4">Warm the original solution and completely precipitate it with H_2S, filter (disregard the filtrate), wash the ppt., transfer it to a dish, boil with HNO_3 (sp. gr. 1.20), and filter.</td></tr>
<tr><td rowspan="3">Ppt. Hg(ic).
Black.</td><td colspan="3">Filtrate Bi, Cu, Cd.
Add NH_4OH in excess and filter.</td></tr>
<tr><td rowspan="2">Ppt. Bi.
White.</td><td colspan="2">Filtrate Cu, Cd.
Blue, if Cu be present. Add H_2S. If the ppt. be yellow, Cd only is present; if dark, filter (disregard the filtrate), wash the ppt., transfer it to a dish, boil with 1 part H_2SO_4 and 10 parts H_2O, and filter.</td></tr>
<tr><td>Ppt. Cu.
Black.</td><td>Filtrate Cd.
Dilute with H_2O and add H_2S.
Yellow ppt.</td></tr>
</table>

NOTES ON THE PRECEDING CHART.

1. Unless excess of H_2S be used, and the solution warmed, Hg will not be thoroughly precipitated.

2. The precipitate of HgS left undissolved upon boiling with HNO_3 is heavy, sinks to the bottom of the dish, and should be black. Upon long boiling, however, it gradually becomes yellow. Sulphur from the sulphides of the bases dissolved by the HNO_3 may be either yellow or black, but is readily distinguished from HgS, because it floats on the liquid. To confirm the presence of Hg, dissolve the precipitate in a mixture of 2 parts HCl and 1 part HNO_3, evaporate carefully to dryness, add H_2O, 2 or 3 drops of HCl, and copper turnings, which, if Hg is present, become coated with globules of that metal.

3. To confirm the presence of Bi, wash the precipitate produced by NH_4OH, treat it with 1 or 2 drops of HCl, and, if necessary, after standing, a few drops of water to displace the liquid from the filter, and allow the solution thus formed to run into a test-tube of water. If Bi is present a white turbidity, due to BiOCl, will result.

CHART FOR THE DETECTION OF BASES IN SOLUTIONS CONTAINING SOLUBLE SALTS OF ALL FOREGOING ELEMENTS.

Hg(ic), Bi, Cu, Cd, As, Sb, Sn, Au, Pt, Fe, Ce, Al, Cr, Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH_4.
Acidify the original solution with HCl, then add H_2S until, after warming, the mixture smells strongly of the reagent, and filter.

- **Ppt. Hg, Bi, Cu, Cd, As, Sb, Sn, Au, Pt.** Wash, digest with $(NH_4)_2S$, filter.
  - **Ppt. Hg, Bi, Cu, Cd.** Wash, boil with HNO_3 (sp. gr. 1.20), filter.
    - **Ppt. Hg.** Black. Confirm by Cu test.
    - **Filt. Bi, Cu, Cd.** Add NH_4OH in excess, and filter.
      - **Ppt. Bi.** White. Confirm by BiOCl test.
      - **Filt. Cu, Cd.** Blue, if Cu be present. Add H_2S. If ppt. be dark, filter (disregard filtrate), wash ppt., boil with 1 part H_2SO_4 and 10 parts H_2O, and filter.
        - **Ppt. Cu.** Black.
        - **Filt. Cd.** Dilute and add H_2S. Yellow ppt.
  - **Filt. As, Sb, Sn, Au, Pt.** Acidify with HCl, agitate, filter (disregard the filtrate), boil the ppt. with strong HCl, filter.
    - **Ppt. As, Au, Pt.** Separate by chart, p. 847.
    - **Filt. Sb, Sn.** Separate by chart, p. 847.
- **Filt. Fe, Ce, Al, Cr, Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH_4.** Add NH_4Cl, NH_4OH, NH_4HS, warm well, and filter.
  - **Ppt. Fe, Ce, Al, Cr, Mn, Zn, Co, Ni.** Wash, dissolve in 2 parts HCl and 1 part HNO_3, evaporate almost to dryness, add H_2O and then NH_4OH in excess, and filter.
    - **Ppt. Fe, Ce, Al, Cr.** Wash, allow to drain, fuse on foil with Na_2CO_3 and KNO_3, boil cooled mass with H_2O, decant upon a filter.
      - **Ppt. Fe, Ce.** Separate according to chart, p. 839.
      - **Filt. Al, Cr.** Yellow, if Cr be present. Divide into two portions.
        - **Al.** Add NH_4Cl, warm well, and allow to stand. White, gelatinous ppt.
        - **Cr.** Acidify with $HC_2H_3O_2$ and add $Pb(A)_2$. Yellow ppt.
    - **Filt. Mn, Zn, Co, Ni.** Acidify slightly with $HC_2H_3O_2$, add H_2S, filter.
      - **Ppt. Zn, Co, Ni.** Wash, dissolve in 2 parts HCl and 1 part HNO_3, evaporate almost to dryness, add H_2O and then KOH until distinctly alkaline, filter.
        - **Ppt. Co, Ni.** Wash, dissolve in HCl, evaporate almost to dryness, add H_2O, and treat with KCN and HCl according to chart, p. 834, then add KOH until alkaline, filter.
          - **Ppt. Ni.** Green. Confirm by borax bead.
          - **Filt. Co.** Evaporate to dryness and test with borax bead.
        - **Filt. Zn.** Add NH_4HS, warm, allow to stand. White ppt.
      - **Filt. Mn.** Add NH_4OH in excess and H_2S. Flesh-colored ppt. Apply Crum's test to original solution.
  - **Filt. Ba, Sr, Ca, Mg, K, Na, Li, NH_4.** Evaporate to remove NH_4HS, add $(NH_4)_2CO_3$, boil, filter.
    - **Ppt. Ba, Sr, Ca.** Wash, dissolve in $HC_2H_3O_2$, dilute, add K_2CrO_4, filter.
      - **Ppt. Ba.** Yellow.
      - **Filt. Sr, Ca.** Add very dilute H_2SO_4, allow to stand, filter.
        - **Ppt. Sr.** White. Confirm by flame test.
        - **Filt. Ca.** Add NH_4OH in excess and $(NH_4)_2C_2O_4$. White ppt.
    - **Filt. Mg, K, Na, Li, NH_4.** Add $(NH_4)_2HPO_4$, agitate, filter.
      - **Ppt. Mg.** White, crystalline.
      - **Filt. K, Na, Li, NH_4.** Add Na_2HPO_4 and NaOH, boil until all NH_3 is expelled, and filter.
        - **Ppt. Li.** White. Confirm by flame test.
        - **Filt. K, Na.** Acidify with $HC_2H_3O_2$, add $Co_2(NO_2)_6 \cdot 6NaNO_2$. Yellow ppt. indicates K.*

---

* Test original solution for K

NOTES ON THE PRECEDING CHART.

1. To digest the sulphides of Groups V. and VI. with $(NH_4)_2S$, it is best to wash the precipitate into a dish, and, after decanting the excess of water and adding the $(NH_4)_2S$, to warm but slightly.

When Sn, Au, and Pt are to be detected, the yellow ammonium sulphide, $(NH_4)_2S$, must be used to insure solution of the sulphides of these bases; but when As and Sb are the only metals of this group to be sought, NH_4HS may be used with equally good results.

2. When Cu is present, some of its sulphide may be dissolved in the process of digesting, so that any dark precipitate obtained upon acidifying the $(NH_4)_2S$ or NH_4HS with HCl should be tested for Cu.

Group VII. Silver, Mercury(ous), Lead.

REACTIONS OF SOLUBLE SALTS OF SILVER.

Use a 1-per-cent. solution of silver nitrate, $AgNO_3$.

1. HCl or a soluble chloride precipitates white, curdy **silver chloride,** AgCl.

$$AgNO_3 + HCl = AgCl + HNO_3.$$

This precipitate is insoluble in HNO_3, but soluble in NH_4OH, forming **ammonio-silver chloride,** $(AgCl)_2(NH_3)_3$.

$$2AgCl + 3NH_4OH = (AgCl)_2(NH_3)_3 + 3H_2O.$$

From this solution AgCl is again precipitated by acidifying with HNO_3.

$$(AgCl)_2(NH_3)_3 + 3HNO_3 = 2AgCl + 3NH_4NO_3.$$

2. H_2S or NH_4HS produces a black precipitate of **silver sulphide,** Ag_2S, soluble in boiling HNO_3.

3. KOH or NaOH forms a grayish-brown precipitate of **silver oxide,** Ag_2O, insoluble in excess of the reagent.

$$2AgNO_3 + 2KOH = Ag_2O + 2KNO_3 + H_2O.$$

4. NH_4OH in small quantity precipitates Ag_2O, soluble in excess of the reagent.

5. K_2CrO_4 produces a red precipitate of **silver chromate,** Ag_2CrO_4, soluble in HNO_3 or NH_4OH.

6. KI and KBr cause respectively precipitates of yellow **silver iodide,** AgI, insoluble in HNO_3 or NH_4OH, and yellowish-

white **silver bromide,** AgBr, insoluble in HNO_3, bu
soluble in NH_4OH.

7. KCN precipitates white **silver cyanide,** AgCN, s
excess of the reagent.

8. Heated with Na_2CO_3 on charcoal, before the blowpi
pounds of silver yield a bright metallic button of **silv**
soluble in HNO_3.

REACTIONS OF SOLUBLE MERCUROUS SALTS.

Use a 1-per-cent. solution of mercurous nitrate, Hg_2(
$2H_2O$.

1. HCl or a soluble chloride precipitates white **me**
chloride, Hg_2Cl_2, converted by strong HNO_3 into a mi
mercuric chloride, $HgCl_2$, and **mercuric nitrate,** Hg
It also becomes black on the addition of NH_4OH, o
formation of **mercurous ammonium chloride,** NH_2H

$$Hg_2Cl_2 + 2NH_4OH = NH_2Hg_2Cl + 2H_2O + N$$

2. H_2S or NH_4HS precipitates a black mixture of **m**
Hg, and **mercuric sulphide,** HgS.

$$Hg_2(NO_3)_2 + H_2S = Hg + HgS + 2HNO$$

3. KOH or NaOH produces a black precipitate of **me**
oxide, Hg_2O, insoluble in excess of the reagent.

4. NH_4OH causes a black precipitate of **mercurous**
nium nitrate, $NH_2Hg_2NO_3$.

5. K_2CrO_4 forms an orange-colored precipitate of **me**
chromate, Hg_2CrO_4.

6. KI precipitates green **mercurous iodide,** Hg_2I_2.

7. Before the blowpipe mercurous salts volatilize, son
converted into a mercuric salt and mercury, both of wh
lime.

REACTIONS OF SOLUBLE SALTS OF LEAD.

Use a 1-per-cent. solution of lead acetate, $Pb(C_2H_3O_2)$,

1. HCl or a soluble chloride produces a white, crystal
cipitate of **lead chloride,** $PbCl_2$, which is quite freely s
hot water, and sparingly in cold.

2. H_2S or NH_4HS precipitates black **lead sulphid**
insoluble in $(NH_4)_2S$ or NH_4HS, but soluble in hot HN

3. KOH or NaOH produces a white precipitate of **le**
drate, $Pb(OH)_2$, soluble in large excess of reagent
potassium or **sodium plumbate,** $Pb(OK)_2$ or Pb(ON

4. NH_4OH precipitates white **basic lead hydrate,** insoluble in excess of the reagent.

5. K_2CrO_4 produces a yellow precipitate of **lead chromate,** $PbCrO_4$, known as **chrome-yellow.** It is soluble in KOH or HNO_3.

6. KI forms a yellow precipitate of **lead iodide,** PbI_2, soluble in boiling water.

7. H_2SO_4 produces a white precipitate of **lead sulphate,** $PbSO_4$, insoluble in acids, except when concentrated and hot, but soluble in $NH_4C_2H_3O_2$ or $(NH_4)_2C_4H_4O_6$.

8. Na_2CO_3 precipitates white **basic lead carbonate,** $(Pb\cdot CO_3)_2Pb(OH)_2$.

9. Before the blowpipe, on charcoal, lead compounds yield a malleable globule of **lead,** Pb, with the formation of an incrustation of yellow **lead oxide,** PbO.

CHART FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP VII.

<table>
<tr><td colspan="3">Completely precipitate the original solution with dilute HCl, filter (disregard the filtrate), wash the ppt. with a small quantity of cold H_2O (disregard the washings also), then pour on the filter boiling H_2O.</td></tr>
<tr><td colspan="2">Precipitate Ag, Hg(ous).
Pour on the filter NH_4OH.</td><td rowspan="2">Filtrate Pb.
Add dilute H_2SO_4 and allow to cool. White ppt.</td></tr>
<tr><td>Ppt. Hg(ous).
Black.</td><td>Filt. Ag.
Acidify with HNO_3.
White, curdy ppt.</td></tr>
</table>

NOTES ON THE FOLLOWING CHART.

1. Before commencing the analysis of a solution, its action on litmus paper must always be noted. If alkaline a precipitate may be caused by HCl, on account of the presence of substances held in solution by alkalies, as, for instance, As_2S_3 in $(NH_4)_2CO_3$, or AgCl in NH_4OH. Silicic acid from alkali silicates may likewise be precipitated; when the latter are present it is necessary to precede the addition of HCl by evaporation to dryness with HNO_3, adding water, filtering out the insoluble silica, and proceeding with the filtrate in the manner described below, commencing with the addition of HCl.

2. Besides causing the precipitation of such substances
mentioned above, HCl more frequently throws down basic sal
of Bi and Sb ; these are, however, readily distinguished from tl
bases of Group VII. by dissolving on the further addition
HCl. Aside from this contingency, the original solution may
turbid from the presence of a precipitate of the bases of Grou
VII., of the basic salts cited, or of some compound decomposab
by HCl.

That no interference or misjudgment may arise from suc
sources as just named, it will be found best before undertakir
the precipitation of the bases of Group VII. to make a prelim
nary test for their presence by adding to a small quantity of tl
original solution an equal volume of dilute HCl. If no precip
tate is produced by this reagent, or if at first formed it is redi
solved, or if originally present it is dissolved, the absence of th
bases of Group VII. is indicated ; in which case, after the add
tion of a few drops of HCl to a larger portion of the origin
solution, the detection of the bases of the first six groups can b
at once proceeded with according to the following chart.

But, on the contrary, if a permanent precipitate is produce
by the equal volume of dilute HCl, or, if originally present, re
mains undissolved, one or more bases of Group VII. are show
to be present ; in which instance the analysis is begun by remov
ing these from a larger portion of the original solution accordin
to the following chart.

3. On account of the slight solubility of $PbCl_2$ in water, P
may be found both in Groups VII. and VI. ; to reduce th
amount held in solution to a minimum the precipitation by HC
should be performed in the cold.

4. When the presence of HNO_3 is suspected, the filtrate, afte
the precipitation of Group VII. and before the addition of H_2S
should be evaporated to dryness to expel the HNO_3. After th
residue has been dissolved in the original bulk of water and acidi
fied with a few drops of HCl, the H_2S may be added and th
analysis continued according to the following chart.

CHART FOR THE DETECTION OF BASES IN SOLUTIONS CONTAINING SOLUBLE SALTS OF ALL FOREGOING ELEMENTS.

Ag, Hg(ous), Pb, Hg(ic), Bi, Cu, Cd, As, Sb, Sn, Au, Pt, Fe, Ce, Al, Cr, Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH_4.

To a small portion of the original solution add an equal volume of dilute HCl. If a ppt. remains undissolved, take a larger portion and add sufficient dilute HCl to completely precipitate it, filter.

<table>
<tr>
<td colspan="3">**Ppt. Ag, Hg(ous), Pb.**
Wash with a very small quantity of cold H_2O, and pour on the filter boiling H_2O.</td>
<td colspan="20">**Filt. Hg(ic), Pb, Bi, Cu, Cd, As, Sb, Sn, Au, Pt, Fe, Ce, Al, Cr, Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH_4.**
Evaporate almost to dryness, add H_2O, acidify with HCl, and then add H_2S until, after warming, the mixture smells strongly of it, filter.</td>
</tr>
<tr>
<td colspan="2">**Ppt. Ag, Hg(ous).**
Pour on the filter NH_4OH.</td>
<td rowspan="6">**Filt. Pb.**
Add dilute H_2SO_4, allow to cool. White ppt.</td>
<td colspan="7">**Ppt. Hg, Pb, Bi, Cu, Cd, As, Sb, Sn, Au, Pt.**
Wash, digest with $(NH_4)_2S$, filter.</td>
<td colspan="13">**Filt. Fe, Ce, Al, Cr, Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH_4.**
Add NH_4Cl, NH_4OH, NH_4HS, warm well, and filter.</td>
</tr>
<tr>
<td rowspan="5">**Ppt. Hg(ous)**
Black.</td>
<td rowspan="5">**Filt. Ag.**
Acidify with HNO_3. White, curdy ppt.</td>
<td colspan="5">**Ppt. Hg, Pb, Bi, Cu, Cd.**
Wash, boil with HNO_3, filter.</td>
<td colspan="2">**Filt. As, Sb, Sn, Au, Pt.**
Acidify with dilute HCl, shake well, filter, disregard filtrate, wash ppt., boil it with strong HCl, filter.</td>
<td colspan="7">**Ppt. Fe, Ce, Al, Cr, Mn, Zn, Co, Ni.**
Wash, dissolve in 2 parts HCl and 1 part HNO_3, evaporate almost to dryness, add H_2O, and then NH_4OH in excess, agitate, and filter.</td>
<td colspan="6">**Filt. Ba, Sr, Ca, Mg, K, Na, Li, NH_4.**
Evaporate to remove NH_4HS, add $(NH_4)_2CO_3$, boil, filter.</td>
</tr>
<tr>
<td rowspan="4">**Ppt. Hg.**
Black. Confirm by Cu test.</td>
<td colspan="4">**Filt. Pb, Bi, Cu, Cd.**
Add two drops of dilute H_2SO_4, evaporate to a small bulk, dilute with H_2O, filter.</td>
<td rowspan="4">**Ppt. As, Au, Pt.**
Separate by chart, page 847.</td>
<td rowspan="4">**Filt. Sb, Sn.**
Separate by chart, page 847.</td>
<td colspan="3">**Ppt. Fe, Ce, Al, Cr.**
Wash, allow to drain, fuse on foil with Na_2CO_3 and KNO_3, boil cooled mass with H_2O, decant upon a filter.</td>
<td colspan="4">**Filt. Mn, Zn, Co, Ni.**
Acidify slightly with $HC_2H_3O_2$, add H_2S, and filter.</td>
<td colspan="3">**Ppt. Ba, Sr, Ca.**
Wash, dissolve in $HC_2H_3O_2$, dilute, add K_2CrO_4, and filter.</td>
<td colspan="3">**Filt. Mg, K, Na, Li, NH_4.**
Add $(NH_4)_2HPO_4$, agitate, and filter.</td>
</tr>
<tr>
<td rowspan="3">**Ppt. Pb.**
White</td>
<td colspan="3">**Filt. Bi, Cu, Cd.**
Add NH_4OH in excess, filter.</td>
<td rowspan="3">**Ppt. Fe, Ce.**
Separate according to chart, page 839.</td>
<td colspan="2">**Filt. Al, Cr.**
Yellow, if Cr be present. Divide into two portions.</td>
<td colspan="3">**Ppt. Zn, Co, Ni.**
Wash, dissolve in HCl and HNO_3, evaporate almost to dryness, add H_2O, and then KOH until alkaline, filter.</td>
<td rowspan="3">**Filt. Mn.**
Add NH_4OH until alkaline and H_2S. Flesh-colored ppt. Apply Crum's test to original solution.</td>
<td rowspan="3">**Ppt. Ba.**
Yellow.</td>
<td colspan="2">**Filt. Sr, Ca.**
Add very dilute H_2SO_4, allow to stand, filter.</td>
<td rowspan="3">**Ppt. Mg.**
White, crystalline.</td>
<td colspan="2">**Filt. K, Na, Li, NH_4.**
Add Na_2HPO_4 and NaOH, boil until all NH_3 is expelled, and filter.</td>
</tr>
<tr>
<td rowspan="2">**Ppt. Bi.**
White. Confirm by BiOCl test.</td>
<td colspan="2">**Filt. Cu, Cd.**
Blue, if Cu be present. Add H_2S; if ppt. be dark, filter, disregard filtrate, wash ppt., boil it with dilute H_2SO_4, filter.</td>
<td rowspan="2">**Al.**
Add NH_4Cl, warm well, and allow to stand. White, gelatinous ppt.</td>
<td rowspan="2">**Cr.**
Acidify with $HC_2H_3O_2$, and add $Pb(\bar{A})_2$. Yellow ppt.</td>
<td colspan="2">**Ppt. Co, Ni.**
Wash, dissolve in HCl, evaporate almost to dryness, add H_2O, treat with KCN and HCl, according to chart, page 834, add KOH until alkaline, filter.</td>
<td rowspan="2">**Filt. Zn.**
Add NH_4HS, warm, allow to stand. White ppt.</td>
<td rowspan="2">**Ppt. Sr.**
White. Confirm by flame test.</td>
<td rowspan="2">**Filt. Ca.**
Add NH_4OH in excess and $(NH_4)_2C_2O_4$. White ppt.</td>
<td rowspan="2">**Ppt. Li.**
Confirm by flame test.</td>
<td>**Filt. K, Na.**
Acidify with $HC_2H_3O_2$, add $Co(NO_2)_6 \cdot 6NaNO_2$. Yellow ppt. indicates K.</td>
</tr>
<tr>
<td>**Ppt. Cu.**
Black.</td>
<td>**Filt. Cd.**
Dilute, add H_2S. Yellow ppt.</td>
<td>**Ppt. Ni.**
Green. Confirm by borax bead.</td>
<td>**Filt. Co.**
Evaporate to dryness and test with borax bead.</td>
<td>Test original solution for Na and NH_4.</td>
</tr>
</table>

CHAPTER II.

THE REACTIONS AND DETECTION OF ACIDS.

Group I. Hydrochloric Acid, Hydrobromic Acid, Hydriodic Acid, Hydrofluoric Acid, Hydrocyanic Acid.

REACTIONS OF SOLUBLE SALTS OF HYDROCHLORIC ACID.

Use a 1-per-cent. solution of potassium chloride, KCl.

1. $AgNO_3$ produces a white, curdy precipitate of **silver chloride**, AgCl, insoluble in HNO_3, but readily soluble in NH_4OH. See reaction No. 1 under silver.

This precipitate should be preserved to compare with the corresponding ones obtained in the reactions of hydrobromic, hydriodic, and hydrocyanic acids.

2. $Hg_2(NO_3)_2$ causes a white precipitate of **mercurous chloride**, Hg_2Cl_2, insoluble in HNO_3, and blackened by the addition of NH_4OH.

3. $Pb(C_2H_3O_2)_2$ forms a white, crystalline precipitate of **lead chloride**, $PbCl_2$, soluble in excess of water.

4. H_2SO_4, warmed with the solution, liberates **hydrochloric acid**, HCl.

$$2KCl + H_2SO_4 = 2HCl + K_2SO_4.$$

This compound may be recognized by its odor and the strongly acid reaction of its vapor, also by the dense, white fumes of NH_4Cl produced by holding a glass rod moistened with NH_4OH near the mouth of the test-tube.

5. H_2SO_4 and MnO_2, added to the solution and the mixture warmed, cause the evolution of **chlorine**, Cl, identified by its odor and color.

$$2KCl + 2H_2SO_4 + MnO_2 = Cl_2 + K_2SO_4 + MnSO_4 + 2H_2O.$$

REACTIONS OF SOLUBLE SALTS OF HYDROBROMIC ACID.

Use a 1-per-cent. solution of potassium bromide, KBr.

1. $AgNO_3$ produces a yellowish-white precipitate of **silver bromide**, AgBr, insoluble in HNO_3, and but very sparingly soluble in NH_4OH.

2. $Hg_2(NO_3)_2$ precipitates yellowish-white **mercurous bromide**, Hg_2Br_2.

3. H_2SO_4 and MnO_2, warmed with the solution, cause the evolution of red vapors of **bromine,** Br, the odor of which is very irritating.

4. Chlorine water liberates Br

$$2KBr + Cl_2 = Br_2 + 2KCl.$$

If starch paste be added to the mixture, a yellow color due to the formation of **starch bromide** results. When this test is applied to very dilute solutions, it is necessary to agitate the mixture with ether or chloroform, which will dissolve the Br, and upon separating from the water will exhibit a yellowish-red color if that element be present.

Reactions of Soluble Salts of Hydriodic Acid.

Use a 1-per-cent. solution of potassium iodide, KI.

1. $AgNO_3$ produces a yellowish precipitate of **silver iodide,** AgI, insoluble in HNO_3 or NH_4OH.

2. $Hg_2(NO_3)_2$ precipitates green **mercurous iodide,** Hg_2I_2.

3. $HgCl_2$ causes a red precipitate of **mercuric iodide,** HgI_2, soluble in an excess of either substance.

4. $Pb(C_2H_3O_2)_2$ produces a yellow precipitate of **lead iodide,** PbI_2, soluble in boiling water.

5. Chlorine water liberates **iodine,** I, which produces with starch paste a blue color of **starch iodide.** The color disappears on heating, but reappears on cooling; it is permanently discharged by an excess of chlorine water, through the formation of colorless **iodine chloride.**

6. $CuSO_4$, in concentrated solution, produces in a solution of KI a white precipitate of **cuprous iodide,** Cu_2I_2, which is colored dark by the iodine set free in the reaction.

$$4KI + 2CuSO_4 = Cu_2I_2 + I_2 + 2K_2SO_4.$$

When, however, a reducing agent, such, for instance, as $FeSO_4$, is added at the same time, the liberation of I is prevented and the true color of the Cu_2I_2 is obtained.

$$2KI + 2CuSO_4 + 2FeSO_4 = Cu_2I_2 + K_2SO_4 + Fe_2(SO_4)_3.$$

Hydrofluoric Acid, HF.

The evolution of intensely irritating fumes, on the addition of H_2SO_4 to calcium fluoride, which etch glass, is sufficiently characteristic of this acid.

REACTIONS OF SOLUBLE SALTS OF HYDROCYANIC ACID.

Use a 1-per-cent. solution of potassium cyanide, KCN.

1. $AgNO_3$ produces a white precipitate of **silver cyanide,** AgCN, soluble in KCN, sparingly soluble in NH_4OH, and insoluble in dilute HNO_3.

2. NH_4HS evaporated with KCN to dryness, at a temperature below boiling, will give, on dissolving the residue in water and adding Fe_2Cl_6, a deep blood-red color of $Fe_2(CNS)_6$, produced from the sulphocyanate formed during the evaporation.

3. $FeSO_4$ and Fe_2Cl_6, when added to the solution and followed with NaOH until a permanent precipitate is produced, will, after heating the mixture and acidifying it with HCl, produce a deep blue precipitate of **ferric ferrocyanide,** $(Fe_2)_2(Fe(CN)_6)_3$.

$$6KCN + FeSO_4 = K_4Fe(CN)_6 + K_2SO_4.$$

$$Fe_2Cl_6 + FeSO_4 + 8NaOH = Fe_2(OH)_6 + Fe(OH)_2 + 6NaCl + Na_2SO_4.$$

$$2Fe_2(OH)_6 + 3K_4Fe(CN)_6 + 12HCl = (Fe_2)_2(Fe(CN)_6)_3 + 12KCl + 12H_2O.$$

4. HCl, HNO_3, or any other acid, causes an evolution of **hydrocyanic acid,** HCN, readily recognized by its odor. Great care should be exercised in carrying out this test in order to avoid inhaling more than a trace of the fumes.

DIRECTIONS FOR THE DETECTION OF THE ACIDS IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP I.

To some of the original solution add a small crystal of $FeSO_4$, some solution of Fe_2Cl_6, and then sufficient NaOH to make the mixture alkaline. Heat and afterwards acidify with HCl; a deep blue precipitate indicates HCN.

If HCN is present, add to another portion of the original solution HNO_3 and boil until all HCN is expelled.

To the solution thus treated, or, when HCN is absent, to some of the original solution simply acidified with HNO_3, add $AgNO_3$; warm the mixture, shake well, and continue the addition of $AgNO_3$ until the precipitation is completed. Collect the precipitate of AgCl, AgBr, and AgI on a filter, wash, and pour upon the filter NH_4OH; AgCl will be dissolved, and may be detected in the filtrate by acidifying with HNO_3. Its presence indicates HCl.

To a third portion of the original solution add a few drops of starch paste, and then, slowly, chlorine water until, after agitation, the liquid smells of it. If a blue color is obtained HI is present. Continue the addition of chlorine water until the blue color is destroyed, when, if the solution is yellow, HBr is indicated. Its presence may be still further verified by agitating the solution with chloroform, which will dissolve the bromine, and upon separating exhibit a yellowish-red color.

NOTE.—Although slight acidity with HCl is not objectionable, alkaline and strongly acid solutions should always be rendered neutral before applying the starch and chlorine test.

Group II. Hypochlorous Acid, Chloric Acid, Hydrosulphuric Acid, Sulphurous Acid, Sulphuric Acid, Thiosulphuric Acid, Nitric Acid, Hypophosphorous Acid, Orthophosphoric Acid, Pyrophosphoric Acid, Metaphosphoric Acid, Boric Acid, Carbonic Acid, Silicic Acid.

REACTIONS OF SOLUBLE SALTS OF HYPOCHLOROUS ACID.

Use a 2-per-cent. solution of sodium hypochlorite, NaClO.

1. HCl causes the evolution of **chlorine,** Cl, readily recognized by its odor and by the bleaching action it exerts on litmus paper or on solution of indigo.

$$NaClO + 2HCl = Cl_2 + NaCl + H_2O.$$

2. $AgNO_3$ produces a white precipitate of **silver chloride,** AgCl, insoluble in HNO_3, but soluble in NH_4OH.

$$3NaClO + 3AgNO_3 = 2AgCl + AgClO_3 + 3NaNO_3.$$

3. $Pb(C_2H_3O_2)_2$, with an excess of the solution, forms at first a white precipitate which, on heating, turns brown, owing to the formation of **lead peroxide,** PbO_2.

$$9NaClO + Pb(C_2H_3O_2)_2 = PbO_2 + 9NaCl + 4CO_2 + 3H_2O.$$

REACTIONS OF SOLUBLE SALTS OF CHLORIC ACID.

Use a 5-per-cent. solution of potassium chlorate, $KClO_3$.

1. H_2SO_4 causes the evolution of yellow **chlorine tetroxide,** having a characteristic odor.

$$3KClO_3 + 2H_2SO_4 = Cl_2O_4 + KClO_4 + 2KHSO_4 + H_2O.$$

When the dry salt is used this reaction takes place with some violence, or, when organic matter is present, with explosion.

2. On heating the dry salt **oxygen,** O, [illegible] and may

be readily detected by holding over the mass the glowing end of a match or taper, which is rekindled by the oxygen.

3. $AgNO_3$ produces no precipitate. This is an important distinction from HCl. When it is present it may be removed by just enough $AgNO_3$ to precipitate it, and the remaining solution after filtration tested for $HClO_3$ by evaporating to dryness, heating to redness, dissolving in water, and adding $AgNO_3$, when, if a chlorate was present, a white precipitate of **silver chloride**, AgCl, will form; the chlorate having been converted by heat into chloride.

$$KClO_3 = KCl + O_3.$$

4. A modification of the above test may be used to distinguish a chlorate from a nitrate, as the latter gives many of the reactions of the former. The residue, after heating a nitrate, will not give a precipitate when dissolved in water and tested with $AgNO_3$.

5. $AgNO_3$, with a drop or two of strong H_2SO_4, will cause a precipitate of AgCl, owing to the decomposition of the chlorate by the strong acid.

HYDROSULPHURIC ACID, H_2S.

Hydrogen Sulphide.

When occurring in moderate amount, sufficient evidence of the presence of this acid is afforded by its characteristic odor. This is at once noticeable in the original material when the acid exists uncombined, but, in the case of sulphides, only after the application of H_2SO_4, and sometimes of heat also.

A trace may be detected by holding over the mouth of the test-tube a piece of filter paper moistened with a drop of solution of lead acetate, when, if H_2S be present, the moistened spot will become black from the formation of lead sulphide.

REACTIONS OF SOLUBLE SALTS OF SULPHUROUS ACID.

Use a 2-per-cent. solution of sodium sulphite, $Na_2SO_3.7H_2O$.

1. In the free state, sulphurous acid, H_2SO_3, may be considered a solution of sulphur dioxide, SO_2, in water, and is recognized by the odor of burning sulphur, which is characteristic of SO_2. The uncombined acid has also strong bleaching action, and readily decolorizes potassium permanganate solution.

$$5H_2SO_3 + K_2Mn_2O_8 = K_2SO_4 + 2MnSO_4 + 2H_2SO_4 + 3H_2O.$$

2. Sulphites are characterized by yielding SO_2 on the addition of a strong acid.

$$Na_2SO_3 + H_2SO_4 = SO_2 + Na_2SO_4 + H_2O.$$

If a piece of filter paper moistened with a drop of lead acetate solution be held over the mouth of the test-tube, no change will occur; but, if this be replaced by one moistened with a drop of mercurous nitrate solution, a blackish color due to metallic **mercury,** Hg, results.

$$4SO_2 + Hg_2(NO_3)_2 + 4H_2O = Hg_2 + 4H_2SO_4 + N_2O_2.$$

3. When the free acid or a sulphite is added to a mixture of zinc and hydrochloric acid, **hydrogen sulphide,** H_2S, is evolved.

$$SO_2 + 3H_2 = H_2S + 2H_2O.$$

4. $BaCl_2$ in neutral solution causes a white precipitate of **barium sulphite,** $BaSO_3$, soluble in HCl.

5. $ZnSO_4$ and $Na_2Fe(NO)(CN)_5$ produce, in dilute solutions of sulphites, a red color, or, in more concentrated solutions, a flocculent reddish precipitate. A few drops of potassium ferrocyanide solution render the reaction more distinct.

REACTIONS OF SOLUBLE SALTS OF SULPHURIC ACID.

Use a 1-per-cent. solution of sodium sulphate, $Na_2SO_4.10H_2O$.

1. $BaCl_2$ produces a white precipitate of **barium sulphate,** $BaSO_4$, insoluble in boiling HCl or HNO_3.

2. $Pb(C_2H_3O_2)_2$ causes a precipitate of white **lead sulphate,** $PbSO_4$, insoluble in dilute acids, but soluble in hot concentrated acids.

3. When a sulphate is fused on charcoal with Na_2CO_3 and the fused mass placed on a bright silver coin and moistened with a drop of dilute HCl, a black stain, due to the formation of **silver sulphide,** Ag_2S, results. This reaction is especially adapted to the detection of insoluble sulphates.

REACTIONS OF SOLUBLE SALTS OF THIOSULPHURIC ACID.

Use a 2-per-cent. solution of sodium thiosulphate, $Na_2S_2O_3.$-$5H_2O$.

1. H_2SO_4 causes the evolution of **sulphur dioxide,** SO_2, and a precipitation of **sulphur,** S; the latter feature distinguishes this acid from sulphurous acid.

$$Na_2S_2O_3 + H_2SO_4 = SO_2 + S + Na_2SO_4 + H_2O.$$

ite precipitate of **silver thios**
excess. After a time (immedia
becomes dark and then black, **sil**
uric acid being formed.

$$\ldots = Ag_2S + H_2SO_4.$$

ite precipitate of **barium thios**
excess of water, and decomposed
sulphur.
zinc and hydrochloric acid, **hyd**
ived.

SOLUBLE SALTS OF NITRIC ACID.

tion of potassium nitrate, KNO_3.
liberates **nitric acid, HNO_3.** If c
with the sulphuric acid, colorless **nitro**
given off, which in contact with air
red **nitrogen tetroxide**, N_2O_4, whic
its color and odor.

$$\ldots = N_2O_2 + 3Cu(NO_3)_2 + 4H_2O;$$
$$N_2O_2 + O_2 = N_2O_4.$$

to the mixture, the characteristic odo
developed.
with H_2SO_4, added in a test-tube, so a
solution of a nitrate acidified with H_2SO_4.
form at the line of contact.
applied in the same manner affords a deep-b

is decolorized by free nitric acid, or b
strongly acidified with H_2SO_4.
nitrate is added to a mixture of zinc and potassi
acid is reduced to **ammonia**, NH_3, whic
may be detected in the usual way.

$$HNO_3 + 4H_2 = NH_3 + 3H_2O.$$

test for distinguishing nitric acid in the p
acid.
on charcoal, deflagration takes place, the charc
expense of the oxygen of the nitrate.

REACTIONS OF SOLUBLE SALTS OF HYPOPHOSPHOROUS ACID.

Use a 2-per-cent. solution of sodium hypophosphite, $NaPH_2O_2.H_2O$.

1. By ignition the hypophosphites are resolved into spontaneously inflammable **hydrogen phosphide,** H_3P, and phosphates.

$$2NaPH_2O_2 = H_3P + Na_2HPO_4.$$

2. $AgNO_3$ produces at first a white precipitate of **silver hypophosphite,** $AgPH_2O_2$, which soon becomes black, owing to the formation of metallic **silver,** Ag.

$$2NaPH_2O_2 + 2AgNO_3 = Ag_2 + 2NaH_2PO_4 + N_2O_2.$$

3. $HgCl_2$ in excess causes a white precipitate of **mercurous chloride,** Hg_2Cl_2. This reaction takes place more rapidly on warming and in the presence of HCl.

$$NaPH_2O_2 + 4HgCl_2 + 2H_2O = 2Hg_2Cl_2 + NaH_2PO_4 + 4HCl.$$

REACTIONS OF SOLUBLE SALTS OF ORTHOPHOSPHORIC ACID.

Use a 2-per-cent. solution of sodium phosphate, $Na_2HPO_4.12H_2O$.

1. $AgNO_3$ causes a light-yellow precipitate of **silver phosphate,** Ag_3PO_4, soluble in HNO_3 or NH_4OH.

2. Fe_2Cl_6, in the presence of sodium acetate, produces a yellowish-white, gelatinous precipitate of **ferric phosphate,** $Fe_2(PO_4)_2$. An excess of Fe_2Cl_6 must be avoided.

3. $(NH_4)_2MoO_4$, in neutral or acid solution, causes a yellow precipitate of **ammonium phosphomolybdate,** $(NH_4)_3PO_4.(MoO_3)_{10}.2H_2O$, to separate slowly. This compound is insoluble in HNO_3, but dissolves in NH_4OH. The precipitation is promoted by the presence of NH_4NO_3, which serves to counteract the tendency of other compounds to retard the formation.

4. Magnesia mixture (consisting of $MgSO_4$, NH_4Cl, and NH_4OH) causes a white precipitate of **magnesium ammonium phosphate,** $Mg(NH_4)PO_4$. Agitation facilitates the formation of this precipitate.

5. $BaCl_2$, in neutral solution, produces a white precipitate of **barium phosphate,** $BaHPO_4$, soluble in HCl.

6. Albumen (white of egg) does not cause a precipitate.

2. $AgNO_3$ produces a white precipitate of **silver thiosulphate,** $Ag_2S_2O_3$, soluble in excess. After a time (immediately on heating) the precipitate becomes dark and then black, **silver sulphide,** Ag_2S, and sulphuric acid being formed.

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4.$$

3. $BaCl_2$ produces a white precipitate of **barium thiosulphate,** BaS_2O_3, soluble in excess of water, and decomposed by HCl with the precipitation of sulphur.

4. Added to a mixture of zinc and hydrochloric acid, **hydrogen sulphide,** H_2S, is evolved.

REACTIONS OF SOLUBLE SALTS OF NITRIC ACID.

Use a 2-per-cent. solution of potassium nitrate, KNO_3.

1. H_2SO_4, on heating, liberates **nitric acid,** HNO_3. If copper turnings be added with the sulphuric acid, colorless **nitrogen dioxide,** N_2O_2, will be given off, which in contact with air absorbs oxygen to form red **nitrogen tetroxide,** N_2O_4, which is readily recognized by its color and odor.

$$8HNO_3 + 3Cu = N_2O_2 + 3Cu(NO_3)_2 + 4H_2O;$$
$$N_2O_2 + O_2 = N_2O_4.$$

If alcohol be added to the mixture, the characteristic odor of nitrous ether is developed.

2. $FeSO_4$, acidified with H_2SO_4, added in a test-tube, so as to form a layer on a solution of a nitrate acidified with H_2SO_4, will cause a dark layer to form at the line of contact.

3. $(C_6H_5)_2NH$ applied in the same manner affords a deep-blue color.

4. Indigo solution is decolorized by free nitric acid, or by a solution of a nitrate strongly acidified with H_2SO_4.

5. When a nitrate is added to a mixture of zinc and potassium hydrate, the nitric acid is reduced to **ammonia,** NH_3, which is vaporized, and may be detected in the usual way.

$$HNO_3 + 4H_2 = NH_3 + 3H_2O.$$

This is a valuable test for distinguishing nitric acid in the presence of chloric acid.

6. Heated on charcoal, deflagration takes place, the charcoal burning at the expense of the oxygen of the nitrate.

REACTIONS OF SOLUBLE SALTS OF HYPOPHOSPHOROUS ACID.

Use a 2-per-cent. solution of sodium hypophosphite, $NaPH_2O_2.H_2O$.

1. By ignition the hypophosphites are resolved into spontaneously inflammable **hydrogen phosphide,** H_3P, and phosphates.

$$2NaPH_2O_2 = H_3P + Na_2HPO_4.$$

2. $AgNO_3$ produces at first a white precipitate of **silver hypophosphite,** $AgPH_2O_2$, which soon becomes black, owing to the formation of metallic **silver,** Ag.

$$2NaPH_2O_2 + 2AgNO_3 = Ag_2 + 2NaH_2PO_4 + N_2O_2.$$

3. $HgCl_2$ in excess causes a white precipitate of **mercurous chloride,** Hg_2Cl_2. This reaction takes place more rapidly on warming and in the presence of HCl.

$$NaPH_2O_2 + 4HgCl_2 + 2H_2O = 2Hg_2Cl_2 + NaH_2PO_4 + 4HCl.$$

REACTIONS OF SOLUBLE SALTS OF ORTHOPHOSPHORIC ACID.

Use a 2-per-cent. solution of sodium phosphate, $Na_2HPO_4.12H_2O$.

1. $AgNO_3$ causes a light-yellow precipitate of **silver phosphate,** Ag_3PO_4, soluble in HNO_3 or NH_4OH.

2. Fe_2Cl_6, in the presence of sodium acetate, produces a yellowish-white, gelatinous precipitate of **ferric phosphate,** $Fe_2(PO_4)_2$. An excess of Fe_2Cl_6 must be avoided.

3. $(NH_4)_2MoO_4$, in neutral or acid solution, causes a yellow precipitate of **ammonium phosphomolybdate,** $(NH_4)_3PO_4.(MoO_3)_{10}.2H_2O$, to separate slowly. This compound is insoluble in HNO_3, but dissolves in NH_4OH. The precipitation is promoted by the presence of NH_4NO_3, which serves to counteract the tendency of other compounds to retard the formation.

4. Magnesia mixture (consisting of $MgSO_4$, NH_4Cl, and NH_4OH) causes a white precipitate of **magnesium ammonium phosphate,** $Mg(NH_4)PO_4$. Agitation facilitates the formation of this precipitate.

5. $BaCl_2$, in neutral solution, produces a white precipitate of **barium phosphate,** $BaHPO_4$, soluble in HCl.

6. Albumen (white of egg) does not cause a precipitate.

Test the reaction ... borates.
alkaline. carbonates.
If the solution is acid. neutralize with ...
separate portions. the following tests, which ser
acids of more frequent occurrence in mixtures:

I. Add some strong H_2SO_4: an odor of SO_2 alone indicate
H_2SO_3. When a precipitate of S accompanies the evolution
SO_2, $H_2S_2O_3$ is present: in which case, to detect H_2SO_3, ap
the next test.

II. Add to some of the original solution sufficient ZnS
completely precipitate it, then a few drops of $Na_2Fe(NO)($
and finally, after mixing, some $K_4Fe(CN)_6$. A red color
if H_2SO_3 is present.

III. Acidify with HCl and add $BaCl_2$; a white precip
dicates H_2SO_4.

IV. Add an equal volume of strong H_2SO_4 and som
turnings, boil: red fumes reveal the presence of HN
firm this test by the other reactions of HNO_3.

V. Evaporate a portion of the original solution t
add a few drops of strong H_2SO_4, stir it well through
add 15 to 20 drops of alcohol, and ignite. In the
copper, a green flame is evidence of H_3BO_3.

VI. Add $HC_2H_3O_2$ or diluted H_2SO_4. An eff
the acid without odor indicates H_2CO_3. When o
given off at the same time, the CO_2 may be identif
into lime water, with which it produces a white
$CaCO_3$.

VII. Acidify a few drops with HNO_3, add i
large quantity of $(NH_4)_2MoO_4$, and warm the
a yellow precipitate is obtained if H_3PO_4 is pre
The salts of the following acids usually oc
other substances. The acids may then be ide

HClO gives with HCl the odor of Cl. It also
... with $AgNO_3$.

$HClO_3$ evolves Cl upon the addition of HCl.
$AgNO_3$ until it has been heated to redness. C
... upon the addition of H_2S
... liberated upon the ... its odor or its action

REACTIONS OF SOLUBLE SALTS OF HYPOPHOSPHOROUS ACID.

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1. By ignition the hypophosphites are resolved into spontaneously inflammable **hydrogen phosphide,** H_3P, and phosphates.

$$2NaPH_2O_2 = H_3P + Na_2HPO_4.$$

2. $AgNO_3$ produces at first a white precipitate of **silver hypophosphite,** $AgPH_2O_2$, which soon becomes black, owing to the formation of metallic **silver,** Ag.

$$2NaPH_2O_2 + 2AgNO_3 = Ag_2 + 2NaH_2PO_4 + N_2O_3.$$

3. $HgCl_2$ in excess causes a white precipitate of **mercurous chloride,** Hg_2Cl_2. This reaction takes place more rapidly on warming and in the presence of HCl.

$$NaPH_2O_2 + 4HgCl_2 + 2H_2O = 2Hg_2Cl_2 + NaH_2PO_4 + 4HCl.$$

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Use a 2-per-cent. solution of sodium phosphate, $Na_2HPO_4.12H_2O$.

1. $AgNO_3$ causes a light-yellow precipitate of **silver phosphate,** Ag_3PO_4, soluble in HNO_3 or NH_4OH.

2. Fe_2Cl_6, in the presence of sodium acetate, produces a yellowish-white, gelatinous precipitate of **ferric phosphate,** $Fe_2(PO_4)_2$. An excess of Fe_2Cl_6 must be avoided.

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4. Magnesia mixture (consisting of $MgSO_4$, NH_4Cl, and NH_4OH) causes a white precipitate of **magnesium ammonium phosphate,** $Mg(NH_4)PO_4$. Agitation facilitates the formation of this precipitate.

5. $BaCl_2$, in neutral solution, produces a white precipitate of **barium phosphate,** $BaHPO_4$, soluble in HCl.

6. Albumen (white of egg) does not cause a precipitate.

OLEIC ACID, $HC_{18}H_{33}O_2$.

Oleic acid is an oily liquid at ordinary temperatures, but becomes solid at 4° C., and remains so until the temperature rises to 14° C., when it again becomes liquid. Lead oleate, $Pb(C_{18}H_{33}O_2)_2$, prepared by saturating sodium oleate with acetic acid and adding lead acetate, is almost entirely soluble in ether. This is an important distinction from stearic acid.

LACTIC ACID, $HC_3H_5O_3$.

Lactic acid is a colorless, odorless, syrupy liquid which has a very sour taste. It is soluble in water, alcohol, and ether, but insoluble in chloroform. When heated with an equal volume of H_2SO_4 and a few crystals of potassium permanganate, a perceptible odor of aldehyde is obtained. Lactates are all soluble in water, though most of them sparingly; they are insoluble in ether.

$Hg_2(NO_3)_2$, boiled with a strong solution of a lactate, yields crimson **mercurous lactate,** $Hg_2(C_3H_5O_3)_2$.

REACTIONS OF SOLUBLE SALTS OF OXALIC ACID.

Use a 4-per-cent. solution of ammonium oxalate, $(NH_4)_2C_2O_4.H_2O$.

1. $K_2Mn_2O_8$, when added to the solution acidified with H_2SO_4, is decolorized.

2. $BaCl_2$ produces a white precipitate of **barium oxalate,** BaC_2O_4, sparingly soluble in $HC_2H_3O_2$ or $H_2C_2O_4$, and freely soluble in HCl, HNO_3, or NH_4Cl.

3. $AgNO_3$ precipitates white **silver oxalate,** $Ag_2C_2O_4$, soluble in hot concentrated HNO_3 and in NH_4OH.

4. $CaCl_2$ produces, even in highly dilute solutions, a white precipitate of **calcium oxalate,** CaC_2O_4, soluble in HCl or HNO_3, but insoluble in $HC_2H_3O_2$.

5. $FeSO_4$, with dilute solutions, causes a yellow color; more concentrated solutions yield, upon warming, a yellow precipitate of **ferrous oxalate,** FeC_2O_4. This compound is insoluble in $HC_2H_3O_2$, but dissolves in HCl or HNO_3.

SUCCINIC ACID, $H_2C_4H_4O_4$.

1. $BaCl_2$ produces no precipitate with a solution of a succinate until alcohol is added, when **barium succinate,** $BaC_4H_4O_4$, which is soluble in NH_4Cl, is thrown down.

2. Fe_2Cl_6 causes a brownish-red, bulky precipitate of **ferric succinate,** $Fe_2(C_4H_4O_4)_3$.

3. $Pb(C_2H_3O_2)_2$ precipitates white, amorphous **lead succinate,** $PbC_4H_4O_4$, soluble in HNO_3.

MALIC ACID, $H_2C_4H_4O_5$.

1. $CaCl_2$ fails to give a precipitate with the acid or its salts until the mixture is boiled, when **calcium malate**, $CaC_4H_4O_5.H_2O$, separates. The addition of alcohol will cause this precipitation without boiling.

2. $Pb(C_2H_3O_2)_2$ precipitates white **lead malate**, $PbC_4H_4O_5.3H_2O$.

REACTIONS OF SOLUBLE SALTS OF TARTARIC ACID.

Use a 2-per-cent. solution of potassium and sodium tartrate, $KNaC_4H_4O_6.4H_2O$.

1. $BaCl_2$ precipitates white **barium tartrate**, $BaC_4H_4O_6$, soluble in ammonium salts or in HCl.

2. $CaCl_2$ produces a white precipitate of **calcium tartrate**, $CaC_4H_4O_6.4H_2O$. Ammonium salts prevent this precipitation. The precipitate is soluble in KOH, from which, upon boiling, it is redeposited. $HC_2H_3O_2$ also dissolves $CaC_4H_4O_6.4H_2O$.

3. $AgNO_3$ causes a white precipitate of **silver tartrate**, $Ag_2C_4H_4O_6$, which becomes black on boiling, owing to the separation of metallic **silver**, Ag. If, however, the precipitate be dissolved in a few drops of NH_4OH, and the solution so obtained be boiled, a mirror of Ag forms on the test-tube. The vessel must be perfectly cleaned for this reaction ; to accomplish this, rinse it with KOH solution and then thoroughly with water.

4. $Ca(OH)_2$ in excess causes a precipitate of **calcium tartrate**, $CaC_4H_4O_6.4H_2O$. This precipitate is flocculent at first, in which state it is readily soluble in NH_4Cl, but after standing for some time it becomes crystalline ; it is then insoluble in NH_4Cl.

5. $H_2C_4H_4O_6$ and tartrates char on heating, and with H_2SO_4 the odor of burnt sugar is given off.

REACTIONS OF SOLUBLE SALTS OF CITRIC ACID.

Use a 2-per-cent. solution of potassium citrate, $K_3C_6H_5O_7.H_2O$.

1. $BaCl_2$ produces a white precipitate of **barium citrate**, $Ba_3(C_6H_5O_7)_2$, soluble in excess of water, in ammonium salts, or in acids.

2. $CaCl_2$ precipitates white **calcium citrate**, $Ca_3(C_6H_5O_7)_2$, when the solutions are boiled together. The precipitate is much more soluble in cold water ; it is also soluble in cold NH_4Cl, but redeposited upon boiling. KOH does not dissolve it.

3. $AgNO_3$ produces a white precipitate of **silver citrate**, $Ag_3C_6H_5O_7$; on boiling no metallic mirror is formed.

DIRECTIONS FOR THE DETECTION OF THE ACIDS IN A SOI TION CONTAINING SOLUBLE SALTS OF GROUP II.

Test the reaction of the original solution with litmus paper ; alkaline, carbonates, borates, and phosphates may be prese If the solution is acid, neutralize with NaOH before applying, separate portions, the following tests, which serve to detect t acids of more frequent occurrence in mixtures :

I. Add some strong H_2SO_4 ; an odor of SO_2 alone indica H_2SO_3. When a precipitate of S accompanies the evolution SO_2, $H_2S_2O_3$ is present ; in which case, to detect H_2SO_3, ap the next test.

II. Add to some of the original solution sufficient $ZnSO_4$ completely precipitate it, then a few drops of $Na_2Fe(NO)(CN$ and finally, after mixing, some $K_4Fe(CN)_6$. A red color resu if H_2SO_3 is present.

III. Acidify with HCl and add $BaCl_2$; a white precipitate dicates H_2SO_4.

IV. Add an equal volume of strong H_2SO_4 and some copp turnings, boil ; red fumes reveal the presence of HNO_3. C firm this test by the other reactions of HNO_3.

V. Evaporate a portion of the original solution to dryne add a few drops of strong H_2SO_4, stir it well through the resid add 15 to 20 drops of alcohol, and ignite. In the absence copper, a green flame is evidence of H_3BO_3.

VI. Add $HC_2H_3O_2$ or diluted H_2SO_4. An effervescence the cold without odor indicates H_2CO_3. When other gases given off at the same time, the CO_2 may be identified by passi it into lime water, with which it produces a white precipitate $CaCO_3$.

VII. Acidify a few drops with HNO_3, add it to a relativ large quantity of $(NH_4)_2MoO_4$, and warm the mixture gentl a yellow precipitate is obtained if H_3PO_4 is present.

The salts of the following acids usually occur unmixed w other substances. The acids may then be identified as follows

HClO gives with HCl the odor of Cl. It also produces a white p cipitate with $AgNO_3$.

$HClO_3$ evolves Cl upon the addition of HCl, but does not precipit $AgNO_3$ until it has been heated to redness. Chlorates deflagrate w charcoal.

H_2S is liberated upon the addition of H_2SO_4 and the application heat. It is recognized by its odor or its action on paper moistened w solution of $Pb(\bar{A})_2$.

HPH_2O_2 is indicated by the odor of H_3P upon strong ignition.

H_4SiO_4 is precipitated as a gelatinous mass when HCl is added to a soluble silicate. To fully confirm this reaction prepare a silica skeleton.

$H_4Fe(CN)_6$ evolves HCN when H_2SO_4 is added and the mixture warmed. Fe_2Cl_6 produces a deep blue precipitate.

$H_6Fe_2(CN)_{12}$ also yields HCN upon treatment with H_2SO_4. It, however, is distinguished from $H_4Fe(CN)_6$ by giving a deep blue precipitate with $FeSO_4$.

$H_4P_2O_7$ causes a white precipitate with $AgNO_3$. By boiling its solution with HNO_3 it is converted into H_3PO_4, which is identified by $(NH_4)_2MoO_4$.

HPO_3 likewise affords a white precipitate with $AgNO_3$. It is changed into H_3PO_4, as is $H_4P_2O_7$; from the latter, however, it differs by producing a precipitate with albumen.

Group III. Acetic Acid, Valerianic Acid, Stearic Acid, Oleic Acid, Lactic Acid, Oxalic Acid, Succinic Acid, Malic Acid, Tartaric Acid, Citric Acid, Carbolic Acid, Benzoic Acid, Salicylic Acid, Gallic Acid, Tannic Acid.

Reactions of Soluble Salts of Acetic Acid.

Use a 2-per-cent. solution of sodium acetate, $NaC_2H_3O_2 \cdot 3H_2O$.

1. In the free state acetic acid is readily recognized by its odor.

2. H_2SO_4, added to an acetate and the mixture warmed, liberates **acetic acid**, $HC_2H_3O_2$.

3. H_2SO_4 and C_2H_5OH in equal volumes, added to an acetate and the mixture warmed, form **acetic ether**, $C_2H_5C_2H_3O_2$, which has a fragrant, slightly acetous odor.

4. Fe_2Cl_6, with a neutral acetate, produces a deep red color, due to **ferric acetate**, $Fe_2(C_2H_3O_2)_6$. This differs from $Fe_2(CNS)_6$ by not being destroyed by $HgCl_2$.

Valerianic Acid, $HC_5H_9O_2$.

The odor is sufficient evidence of the presence of this acid. This odor is developed by moisture and heat, and in the case of the salts by the addition of H_2SO_4.

Stearic Acid, $HC_{18}H_{35}O_2$.

Stearic acid is a white, fatty solid, melting at 69.2° C., giving when combined with potassium a soft soap, and with sodium a hard soap; from both it separates as an oily liquid on the addition of HCl, becoming solid on cooling. The lead salt, lead stearate, $Pb(C_{18}H_{35}O_2)_2$, is insoluble in ether.

Oleic Acid, $HC_{18}H_{33}O_2$.

Oleic acid is an oily liquid at ordinary temperatures, but becomes solid at 4° C., and remains so until the temperature rises to 14° C., when it again becomes liquid. Lead oleate, $Pb(C_{18}H_{33}O_2)_2$, prepared by saturating sodium oleate with acetic acid and adding lead acetate, is almost entirely soluble in ether. This is an important distinction from stearic acid.

Lactic Acid, $HC_3H_5O_3$.

Lactic acid is a colorless, odorless, syrupy liquid which has a very sour taste. It is soluble in water, alcohol, and ether, but insoluble in chloroform. When heated with an equal volume of H_2SO_4 and a few crystals of potassium permanganate, a perceptible odor of aldehyde is obtained. Lactates are all soluble in water, though most of them sparingly; they are insoluble in ether.

$Hg_2(NO_3)_2$, boiled with a strong solution of a lactate, yields crimson **mercurous lactate,** $Hg_2(C_3H_5O_3)_2$.

Reactions of Soluble Salts of Oxalic Acid.

Use a 4-per-cent. solution of ammonium oxalate, $(NH_4)_2C_2O_4.H_2O$.

1. $K_2Mn_2O_8$, when added to the solution acidified with H_2SO_4, is decolorized.

2. $BaCl_2$ produces a white precipitate of **barium oxalate,** BaC_2O_4, sparingly soluble in $HC_2H_3O_2$ or $H_2C_2O_4$, and freely soluble in HCl, HNO_3, or NH_4Cl.

3. $AgNO_3$ precipitates white **silver oxalate,** $Ag_2C_2O_4$, soluble in hot concentrated HNO_3 and in NH_4OH.

4. $CaCl_2$ produces, even in highly dilute solutions, a white precipitate of **calcium oxalate,** CaC_2O_4, soluble in HCl or HNO_3, but insoluble in $HC_2H_3O_2$.

5. $FeSO_4$, with dilute solutions, causes a yellow color; more concentrated solutions yield, upon warming, a yellow precipitate of **ferrous oxalate,** FeC_2O_4. This compound is insoluble in $HC_2H_3O_2$, but dissolves in HCl or HNO_3.

Succinic Acid, $H_2C_4H_4O_4$.

1. $BaCl_2$ produces no precipitate with a solution of a succinate until alcohol is added, when **barium succinate,** $BaC_4H_4O_4$, which is soluble in NH_4Cl, is thrown down.

2. Fe_2Cl_6 causes a brownish-red, bulky precipitate of **ferric succinate,** $Fe_2(C_4H_4O_4)_3$.

3. $Pb(C_2H_3O_2)_2$ precipitates white, amorphous **lead succinate,** $PbC_4H_4O_4$, soluble in HNO_3.

MALIC ACID, $H_2C_4H_4O_5$.

1. $CaCl_2$ fails to give a precipitate with the acid or its salts until the mixture is boiled, when **calcium malate**, $CaC_4H_4O_5.H_2O$, separates. The addition of alcohol will cause this precipitation without boiling.

2. $Pb(C_2H_3O_2)_2$ precipitates white **lead malate**, $PbC_4H_4O_5.3H_2O$.

REACTIONS OF SOLUBLE SALTS OF TARTARIC ACID.

Use a 2-per-cent. solution of potassium and sodium tartrate, $KNaC_4H_4O_6.4H_2O$.

1. $BaCl_2$ precipitates white **barium tartrate**, $BaC_4H_4O_6$, soluble in ammonium salts or in HCl.

2. $CaCl_2$ produces a white precipitate of **calcium tartrate**, $CaC_4H_4O_6.4H_2O$. Ammonium salts prevent this precipitation. The precipitate is soluble in KOH, from which, upon boiling, it is redeposited. $HC_2H_3O_2$ also dissolves $CaC_4H_4O_6.4H_2O$.

3. $AgNO_3$ causes a white precipitate of **silver tartrate**, $Ag_2C_4H_4O_6$, which becomes black on boiling, owing to the separation of metallic **silver**, Ag. If, however, the precipitate be dissolved in a few drops of NH_4OH, and the solution so obtained be boiled, a mirror of Ag forms on the test-tube. The vessel must be perfectly cleaned for this reaction; to accomplish this, rinse it with KOH solution and then thoroughly with water.

4. $Ca(OH)_2$ in excess causes a precipitate of **calcium tartrate**, $CaC_4H_4O_6.4H_2O$. This precipitate is flocculent at first, in which state it is readily soluble in NH_4Cl, but after standing for some time it becomes crystalline; it is then insoluble in NH_4Cl.

5. $H_2C_4H_4O_6$ and tartrates char on heating, and with H_2SO_4 the odor of burnt sugar is given off.

REACTIONS OF SOLUBLE SALTS OF CITRIC ACID.

Use a 2-per-cent. solution of potassium citrate, $K_3C_6H_5O_7.H_2O$.

1. $BaCl_2$ produces a white precipitate of **barium citrate**, $Ba_3(C_6H_5O_7)_2$, soluble in excess of water, in ammonium salts, or in acids.

2. $CaCl_2$ precipitates white **calcium citrate**, $Ca_3(C_6H_5O_7)_2$, when the solutions are boiled together. The precipitate is much more soluble in cold water; it is also soluble in cold NH_4Cl, but redeposited upon boiling. KOH does not dissolve it.

3. $AgNO_3$ produces a white precipitate of **silver citrate**, $Ag_3C_6H_5O_7$; on boiling no metallic mirror is formed.

4. $Ca(OH)_2$, in excess, does not cause a precipitate until mixture is boiled. This is an important distinction from tart acid.

5. $H_3C_6H_5O_7.H_2O$ and citrates char on heating, and v H_2SO_4 give off the odor of burnt sugar.

CARBOLIC ACID, C_6H_5OH.

1. HNO_3, with an aqueous solution of the acid, forms a yellow c due to the formation of **picric acid**, $C_6H_2(NO_2)_3OH$.

2. Fe_2Cl_6 produces a **violet-blue** color.

3. A piece of pine wood dipped in the acid and then exposed to fumes of HCl becomes, after a short time, colored **blue.**

4. Bromine water causes a white precipitate of **tribromphenol,** C_6 Br_3OH, which, under the microscope, appears crystalline.

5. Albumen or collodion is **coagulated** by carbolic acid.

REACTIONS OF BENZOIC ACID, $HC_7H_5O_2$.

1. Fe_2Cl_6 precipitates from neutral solutions flesh-colored f **ric benzoate,** $Fe_2(C_7H_5O_2)_6$, decomposable by HCl with separation of $HC_7H_5O_2$.

2. HCl causes the separation of $HC_7H_5O_2$ from cold soluti of the benzoates.

3. $BaCl_2$ and $CaCl_2$ produce no precipitates with either free acid or its salts.

4. $HC_7H_5O_2$ is soluble in petroleum ether; the latter solv removes the acid from its aqueous solution when agitated th with.

5. Heated in a test-tube with freshly slaked lime, benzoic a yields **benzol,** C_6H_6, recognizable by its odor.

6. The pure acid melts at 121.4°.

REACTIONS OF SALICYLIC ACID, $HC_7H_5O_3$.

1. Fe_2Cl_6 produces a deep **violet** color, which is very char teristic.

2. Warmed with H_2SO_4 and CH_3OH, the fragrant odor **methyl salicylate,** $CH_3C_7H_5O_3$, is developed.

3. HCl causes the separation of $HC_7H_5O_3$ from cold soluti of the salicylates.

4. $HC_7H_5O_3$ is insoluble in petroleum ether. Advantage taken of this fact to separate benzoic and salicylic acids wh mixed.

5. The pure acid melts at 156° to 157°.

REACTIONS OF GALLIC ACID, $HC_7H_5O_5.H_2O$.

1. $FeSO_4$ causes no change in color.

2. Fe_2Cl_6 produces a bluish-black precipitate, which disappears on heating.

3. KOH or NaOH, if not in excess, develops slowly a deep green color, which becomes red on the addition of acids. Alkali carbonates cause the same green color, although more slowly.

4. No precipitate is produced with either gelatin or the alkaloids. With the former, however, a precipitation takes place when gum is present.

REACTIONS OF TANNIC ACID, $C_{14}H_{10}O_9$.

Gallotannic Acid.

1. $FeSO_4$, when perfectly pure, causes no change. In the presence of oxygen, however, a dark color rapidly develops; this, on standing, slowly becomes a precipitate.

2. Fe_2Cl_6 produces a bluish-black precipitate. An excess gives a green color because of the acid usually present in the reagent.

3. $Fe_2(NH_4)_2(SO_4)_4$ affords the same color and precipitate, and, as it contains no free acid, constitutes a better reagent than Fe_2Cl_6.

4. Test solution of iodine mixed with a small quantity of ammonium hydrate, previously diluted with ten times its volume of water, produces a brilliant red color. This reaction will take place with only traces of tannic acid.

5. Gelatin causes a white, flocculent precipitate. This reaction is more delicate in the presence of alum.

6. Alkaloids produce white precipitates, soluble in acetic acid and in alcohol.

7. $K(SbO)C_4H_4O_6$ causes a white, gelatinous precipitate. Most other metallic salts likewise give precipitates.

DIRECTIONS FOR THE DETECTION OF THE ACIDS IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP III.

As many of the acids in this group would indicate their presence by odor or physical appearance, a method of separating only the more important and closely related ones will be given.

The list will, therefore, be limited to Acetic Acid, Oxalic Acid, Tartaric Acid, and Citric Acid.

The solution should be neutral to litmus paper; if acid, neutralize with NaOH, if alkaline, with HNO_3.

To a small portion add an equal volume each of strong H_2SO_4 and C_2H_5OH and warm. Acetic acid will, if present, be indicated by the odor of acetic ether.

Make another portion slightly alkaline with NH_4OH, add $CaCl_2$, allow to stand (avoiding heat) for ten minutes, and filter (make sure the precipitation has been complete).

<table>
<tr><td colspan="2">**Ppt. $H_2C_2O_4$, $H_2C_4H_4O_6$.**
Wash, pour on the filter $HC_2H_3O_2$.</td><td rowspan="2">**Filt. $H_3C_6H_5O_7$.**
Boil to expel all NH_4OH. White ppt. slowly forming on the sides of the tube indicates $H_3C_6H_5O_7$.</td></tr>
<tr><td>**Ppt. $H_2C_2O_4$.**
Confirm by testing the original solution with $HC_2H_3O_2$ and $CaCl_2$.</td><td>**Filt. $H_2C_4H_4O_6$.**
Add NH_4OH until slightly alkaline. White ppt. Confirm by forming mirror with $AgNO_3$ in original solution.</td></tr>
</table>

CHAPTER III.

THE DETECTION OF BASES AND ACIDS.

SPECIAL OBSERVATIONS.

THE bases must always be determined first in a portion of the solution or powder, according to chart, page 859.

Besides the substances mentioned in the precautions on page 858, certain acids, when present in combination, as, for instance, benzoic and salicylic, are also precipitated from their salts by HCl; in such cases it is first necessary to evaporate the solution to dryness and heat to redness before proceeding with the detection of bases.

When phosphates are present in acid solution (determined by adding a few drops of the solution to some NH_4NO_3 and $(NH_4)_2MoO_4$ and warming), the chart on page 878 must be used in the analysis of the precipitate of Group IV., as, in addition to Fe, Ce, Al, Cr, there may be present the phosphates of Ca, Sr, Ba, Mn, Mg. The addition of Na_2HPO_4 is to insure the formation of the phosphates of Fe, Ce, Al, Cr. The $NH_4C_2H_3O_2$ should be freshly prepared by adding $HC_2H_3O_2$ to NH_4OH until the solution is slightly acid. The presence of oxalates would likewise necessitate an exception to the general chart for the detection of bases; when present, therefore, the substance must be heated to redness before commencing the analysis.

When the analysis of a solid is to be performed, all of its physical properties should be carefully observed. The action on litmus paper of the portion soluble in water is also to be noted, and the solution made neutral if necessary.

If only the alkali metals are present and the reaction is neutral, proceed to search for the acids according to Division I. If the reaction is acid or alkaline, neutralize as directed in Division II.

If other than the alkali metals are present, and the reaction is acid, conduct the detection of the acids according to Division II.

When the substance is not entirely dissolved by H_2O, HCl, or a mixture of HCl and HNO_3, proceed for both bases and acids according to Division III.

CHART FOR THE ANALYSIS OF THE PRECIPITATE OF GROUP IV. WHEN PHOSPHATES ARE PRESENT.

<table>
<tr><td colspan="6">Dissolve the precipitate in HCl, add Na_2HPO_4, then excess of $NH_4C_2H_3O_2$, boil, and filter.</td></tr>
<tr><td colspan="2">Ppt. Fe. Ce. Al.
Wash with hot H_2O, then pour on the filter hot solution of KOH.</td><td colspan="4">Filt. Ba, Sr, Ca, Mn, Mg, Cr (Green, if Cr be present).
Add K_2CrO_4, warm, and filter.</td></tr>
<tr><td rowspan="3">Ppt. Fe. Ce.
Wash, dissolve in HCl. Test a portion with $K_4Fe(CN)_6$ or [illegible].
Blue ppt.
Confirm in original solution.

To another portion add $H_2C_4H_4O_6$, NH_4OH in excess and Na_2HPO_4.
White ppt. indicates Ce.</td><td rowspan="3">Filt. Al.
Acidify with $HC_2H_3O_2$.
White ppt.</td><td rowspan="3">Ppt. Ba.
Yellow.</td><td colspan="3">Filt. Sr, Ca, Mn, Mg.
Add very dilute H_2SO_4, allow to stand, filter. An excess of H_2SO_4 should be avoided.</td></tr>
<tr><td rowspan="2">Ppt. Sr.
White. Confirm by flame test.</td><td colspan="2">Filt. Ca, Mn, Mg.
Add $NH_4C_2H_3O_2$ and $(NH_4)_2C_2O_4$, filter.</td></tr>
<tr><td>Ppt. Ca.
White.</td><td>Filt. Mn, Mg.
Evaporate a portion to dryness and test with borax bead for Mn. To the remaining portion add Fe_2Cl_6, filter out the $Fe_2(PO_4)_2$, to the filtrate add NH_4Cl, NH_4OH, and NH_4HS, to remove Fe and Mn, filter, and test filtrate with Na_2HPO_4.
White, crystalline ppt. indicates Mg.</td></tr>
</table>

DIVISION I. When the bases are the alkali metals, and the reaction of the solution is neutral.

RULE I.—*Evaporate a portion of the solution to dryness and slowly heat to redness.*

If the mass char, one or more of the following salts of organic acids are indicated: **Acetates, Lactates, Succinates, Malates, Tartrates, Citrates, Benzoates, Salicylates, Gallates, Tannates. Oxalates** do not char, although if the heating take place slowly a grayish coloration may be noticed. The residues in all these cases give off CO_2 on the addition of H_2SO_4.

Fe_2Cl_6, added to the original solution, usually detects **Benzoates, Salicylates, Gallates,** and **Tannates.** When unmixed, the color obtained will distinguish the first two. Benzoic and salicylic acids are precipitated upon acidifying the solution. They may be removed from their water solution by shaking with ether, and afterwards separated by the use of petroleum ether; both the soluble and insoluble portions should then be further tested with the reagents given under the reactions of these acids. Gallic and tannic acids give with Fe_2Cl_6 precipitates of the same color. Upon agitating the water solution with ether, gallic acid is dissolved, and, upon separating and evaporating the solvent, may be identified by the usual reagents for that acid.

Tannic acid differs from gallic acid by being more soluble in water, and by this solution producing a precipitate with gelatin.

The detection of the organic acids of more common occurrence is conducted according to the chart on page 876.

The physical properties of the salts of the other organic acids will usually aid in their recognition by the tests given in the consideration of them.

RULE II.—*Evaporate another portion to dryness, allow the residue to cool, add a few drops of strong* H_2SO_4, *warm gently, and note any of the following effects which may ensue from this single reaction:*

Effervescence in the cold, no odor	Carbonates.	Confirm in original solution by dilute acid.
Effervescence on heating, odor of H_2S	Sulphides . . .	Confirm by adding acid to original solution.
Odor of SO_2	Sulphites . . .	
Odor of SO_2 with separation of S	Thiosulphates .	
Dark-brown color and violet fumes	Iodides.	Confirm by starch and Cl water.
Dark-red color and reddish fumes	Bromides.	Confirm by starch and Cl water.
Odor of HCN	Cyanides, Ferro- or Ferri-Cyanides.	Confirm in original solution.
Odor of $HC_2H_3O_2$	Acetates.	Confirm by acetic ether test.
Odor of Cl	Hypochlorites.	
Odor of Cl_2O_4	Chlorates.	
Strongly acid suffocating fumes	Chlorides.	Confirm by $AgNO_3$.
Strongly acid fumes, odor of N_2O_4	Nitrates.	Confirm by other tests.
Characteristic odors . . .	Benzoates, Succinates, Valerianates, Carbolates, Hypophosphites.	

RULE III.—*Acidify a third portion with* HCl *and add* $BaCl_2$.

A white precipitate indicates **Sulphates.**

RULE IV.—*To a fourth portion add* $CaCl_2$.

A white precipitate soluble in excess of H_2O indicates **Sulphates**; if insoluble in excess of H_2O or $HC_2H_3O_2$, **Oxalates** are indicated. A white precipitate, soluble in KOH and reprecipitated upon boiling, indicates **Tartrates**; the latter test should be confirmed by forming a mirror of silver on the test-tube. A white precipitate, soluble in NH_4Cl and reprecipitated upon boiling, indicates **Citrates.**

For further instruction regarding the separation of these acids consult the chart on page 876.

When **Sulphates** are present it is important to remove them before attempting the detection of **Oxalates, Tartrates,** and **Citrates** by the use of $CaCl_2$. To accomplish this, treat the solution with HCl and $BaCl_2$, filter off the $BaSO_4$, neutralize the filtrate with NaOH, and proceed according to the chart on page 876.

RULE V.—*Acidify a fifth portion with* HNO_3 *and add* $AgNO_3$ *until the precipitation is completed.*

Collect the precipitate, wash it, and pour upon the filter NH_4OH. Acidify the filtrate so obtained with HNO_3; a white precipitate indicates **Chlorides.** When **Cyanides** are present they must be removed by boiling with HNO_3 before adding the $AgNO_3$.

RULE VI.—*Add to a sixth portion of the solution starch paste and chlorine water.*

A blue color indicates **Iodides.** Continue the addition of chlorine water until the blue color of starch iodide is discharged, then shake with chloroform. A yellowish-red color is imparted to this solvent if **Bromides** are present.

For fuller directions, see page 862.

RULE VII.—*Add a few drops of the solution to a relatively large quantity of* $(NH_4)_2MoO_4$ *and warm.*

Phosphates and **Arsenates** produce yellow precipitates. The presence or absence of As is always ascertained in the detection of bases. When present, it should be separated from another portion of the solution by HCl and H_2S; the filtrate, afte boiling to expel H_2S, is then neutralized with NH_4OH an treated with magnesia mixture. A white crystalline precipitate confirms the presence of **Phosphates.**

The detection of **Pyrophosphates** and **Metaphosphates** may be conducted by the directions given on page 871.

RULE VIII.—*To an eighth portion apply the special test with* H_2SO_4 *and* $FeSO_4$ *for* **Nitrates.**

A dark layer at the line of contact reveals their presence.

RULE IX.—*To some of the dry salt, or to the residue obtained by evaporating a portion of the solution to dryness, add a few drops of strong* H_2SO_4 *and 15 or 20 drops of alcohol, mix well, and apply flame.* **Borates,** *if present, will impart a green color to the flame of the burning alcohol.*

Chromates, Manganates, and **Permanganates,** when present, impart color to the solution. The metals from which their acid radicals arise will be ascertained in the detection of bases. The characters of these salts have been previously discussed under different reactions, which may be employed to more fully establish the presence of their constituent acids.

DIVISION II. When the solution is acid to litmus paper, or when the substance to be analyzed is a solid which requires the use of acid to dissolve it.

After determining the bases by the chart on page 859 (bearing in mind the exception in regard to phosphates) a portion of the material is tested according to Rules I and II, **DIVISION I.**

A second portion of the solution is then to be treated as follows:

Boil with sufficient solution of Na_2CO_3 to make the mixture alkaline.		
Ppt. consists of the carbonates, hydrates, and oxides of the bases present, and is disregarded.	Filt. contains the acids in the form of salts of Na. Divide into two portions.	
	To one portion add HCl until slightly acid, boil to remove CO_2, neutralize with NaOH, and test according to Rules III, IV, VI, VIII, and IX, DIVISION I.	To another portion add HNO_3 until slightly acid, boil to remove CO_2, neutralize with NaOH, and test according to Rules V and VII, and if necessary III, IV, VI, and IX, DIVISION I.

When heavy metals are present Rule I, Division I, is preferably applied to the filtrate after boiling with Na_2CO_3; the portion neutralized with HCl and NaOH is recommended for use in all such cases. Rule II should be invariably performed on the original solution or solid. When Cu is present it is best to add, along with the Na_2CO_3, some NaOH to insure the complete precipitation of that base.

Hydrates and Oxides.

When, in the analysis of an inorganic substance for acids, negative results are obtained, the material under consideration may be either a hydrate or an oxide.

The hydrates of K, Na, Li, Ca, Sr, and Ba are soluble in water, and yield solutions which change red litmus paper blue. The hydrates of other metals are insoluble in water. These, as also the hydrates of Ca, Sr, and Ba, when heated in a dry test-tube, give off vapor of water which condenses on the cooler part of the tube; it is characterized by having no odor or taste, and by not changing the color of litmus paper.

Oxides do not yield water when thus heated. The oxides of K, Na, Li, Ca, Sr, and Ba dissolve in water to form hydrates; the oxides of other metals are insoluble in water.

DIVISION III. When the substance is not entirely dissolved by H_2O, HCl, or a mixture of HCl and HNO_3.

Add water and filter; the filtrate, if it contain solid matter (determined by evaporating a small quantity to dryness), is examined for bases by the chart on page 859, and for acids by Division I. The residue, after treatment with water, is treated with HCl, or, if necessary, with a mixture of HCl and HNO_3. Any bases that may be dissolved are detected by the chart on page 859, while the acids are determined according to Division II. The insoluble residue consists of one or more of the following substances: Sulphates of Ba, Sr, Ca, Pb; Chlorides, Bromides, and Iodides of Ag, Pb; certain Oxides which have been highly heated, as Fe_2O_3, Al_2O_3, Cr_2O_3, SnO_2; Silica and Silicates; Carbon and Sulphur (the last two are readily detected in the preliminary examination by heat). This residue is mixed with about four times its weight of dry Na_2CO_3, and fused on a platinum foil; the mass is boiled with water, and the soluble portion examined for acids according to Division II. The portion undissolved by water is treated with HCl; the solution so obtained evaporated to dryness, the residue dissolved in water with the aid of a little HCl, and examined for bases by the chart on page 859. Special attention should be given to the notes preceding this chart. If, after fusing with Na_2CO_3, the metals lead and silver are present in the residue insoluble in water and HCl, they can best be determined by dissolving such portions in HNO_3 and proceeding with the analysis as directed in Division II. Many of these insoluble substances are detected in a preliminary examination by the use of the blowpipe, as explained in the reactions given under the individual elements.

The Analysis of Alloys.

The following general outline suffices for the examination of the more common alloys:

Pour over the substance HNO_3, sp. gr. 1.20, and evaporate to dryness with a moderate heat. This treatment converts most of the metals into nitrates, which are soluble in water or very weak HNO_3; Sb and Sn are, however, changed to oxides, which are insoluble in water or HNO_3, while Pt and Au remain unaltered in the metallic state, and hence fail to dissolve in the same liquids.

The residue obtained upon evaporating to dryness is treated with water containing a small amount of HNO_3 to insure the solution of bismuth; the mixture is then filtered, and the analysis of the filtrate conducted according to the chart on page 859. The oxides of Sb and Sn may be separated from the metallic Pt and Au by warming with strong HCl; after filtration the Sb and Sn are separated by the chart on page 847.

Pt and Au may be identified by dissolving in a mixture of HCl and HNO_3, and applying the tests given in the chart on page 847.

SECTION II.

QUANTITATIVE ANALYSIS.

CHAPTER I.

GRAVIMETRIC PROCESSES.

IN the following short course in gravimetric operations a few typical salts are given for estimation, with the belief that a thorough knowledge of the operations involved in these will enable the learner to carry out most of the processes he will be called on to perform in inorganic work.

Before undertaking this section the student should be thoroughly familiar with the preceding qualitative operations, and it is especially desirable at this point that he should have instruction from some one familiar with the use of analytical balances and weights. In addition, the following rules should be kept constantly in mind by those using a fine balance :

1. Never put any chemical substance directly on the pan of a balance, but first weigh a clean, dry crucible or watch crystal, and then weigh the substance in it.
2. Never put on or take off a weight, or anything else, from a balance when the beam is resting on the knife-edges.
3. All weights should be transferred in regular order, and the forceps always used instead of the fingers.
4. Volatile acids, and all other corrosive substances, like chlorine water, iodine, or solution of ammonia, should be weighed in stoppered weighing-tubes or small test-tubes with closely fitting corks.
5. The door of the balance should be kept open no longer than is absolutely necessary.

In addition to the above rules, it may be said that most substances and containers, that are heated previous to weighing, should be cooled in a desiccator.

Before beginning quantitative operations the student should provide himself with a note-book, to be used for this purpose only, and in which he should keep a record of all weighings in a systematic manner, so they may be referred to on short notice.

Precipitation.—When a substance has been weighed it is usually first dissolved, the solvent depending on the nature of the material under investigation. This is generally followed by precipitation, which should be conducted in beaker glasses, or, in a few cases, when an alkaline liquid is to be boiled, for instance, in porcelain evaporating dishes.

In precipitation, an excess of the reagent should be avoided, except in a few cases where it is especially directed. The filtrate should always be tested with a few more drops of the reagent to determine that the precipitation has been complete.

Distilled water should be employed in all quantitative operations.

Filtration.—Filter paper having a very small ash should be employed. That known in commerce as Swedish No. 2 will be found satisfactory for most purposes.

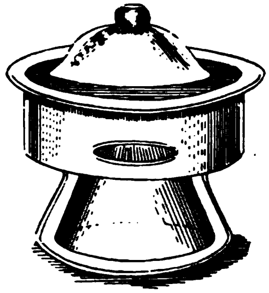
Plain filters should always be used. They are made by folding a circular piece of the paper twice, and then opening so as to form a cone, which will exactly fit into a 60° funnel, so that the liquid will pass out at the point of the cone, instead of escaping at the sides. By this means a precipitate can be more thoroughly washed, and in a shorter time.

The filter should be of such size that it will not project above the edge of the funnel.

The precipitate should be allowed to settle in the vessel after it is formed. The clear, supernatant liquid is then to be transferred to a filter by pouring it down a glass rod held against the lip of the beaker to conduct it into the filter without loss.

The precipitate is then washed into the filter with the aid of a jet from a wash-bottle, and the washing continued until, by the appropriate test, it is found to be complete. The washing, in many cases, is to be done with hot water.

FIG. 111.



Desiccator.

Drying.—The filter and its contents may be dried in the funnel, set in a warm place, or they may be removed from the funnel, placed on a watch crystal or in a crucible, and dried in an air-bath, at any suitable temperature.

Ignition.—This is usually performed in a platinum or porcelain crucible, the precipitate in some cases being separated from the filter, and the latter burned separately on the crucible lid; then placed in the crucible with the precipitate, and the whole brought to low or bright redness as is required. It is then allowed to cool in a desiccator, Fig. 111, until nearly the temperature of the balance-room, when it is ready for weighing.

EXAMPLES FOR PRACTICE BY GRAVIMETRIC PROCESSES.

BARIUM CHLORIDE, $BaCl_2.2H_2O$.

Estimation of the Barium.

About 0.500 gramme of the pure salt are weighed, and dissolved in 100 c.c. of water, in a beaker of about 200 c.c. capacity. Dilute sulphuric acid is added, drop by drop, as long as any precipitate is produced, and the mixture then boiled. The precipitate is allowed to settle, the clear, supernatant liquid poured down a glass rod into a filter, the precipitate is boiled with a fresh quantity of water, and, after pouring in the clear liquid, transferred to the filter.

The small portions of the precipitate which adhere to the sides of the beaker are removed with a glass rod having on its end a short section of closely fitting rubber tubing. The precipitate is washed with hot water until the washings cease to cause a turbidity with solution of barium chloride; it is then dried, ignited, and weighed as barium sulphate, $BaSO_4$.

Suppose we have taken 0.475 gramme of barium chloride, and find 0.455 gramme of barium sulphate, we have:

Molecular Wt. of $BaSO_4$.		Atomic Wt. of Ba.		Wt. of $BaSO_4$ found.		Wt. of Ba found.
232.72	:	136.90	: :	0.455	:	0.267+

Having determined the amount of barium found, we make another proportion in order to calculate the percentage found, that we may compare it with the theoretical percentage in the barium chloride:

Wt. of $BaCl_2.2H_2O$ taken.		Wt. of Ba found.				Per cent. of Ba found.
0.475	:	0.267+	: :	100	:	56.21

The theoretical percentage of barium is ascertained as follows:

Molecular Wt. of $BaCl_2.2H_2O$.		Atomic Wt. of Ba.				Per cent. of Ba.
243.56	:	136.90	: :	100	:	56.21

By substituting the atomic weight of the barium by the molecular weight of the chlorine or of the water in the foregoing proportion the percentage of either of these constituents may be computed.

Ba = 136.90 = 56.21 per cent.
Cl_2 = 70.74 = 29.04 "
$2H_2O$ = 35.92 = 14.75 "
243.56 100.00

Estimation of the Chlorine.

To determine the percentage of this constituent of barium chloride, another portion of the salt, about 0.200 gramme, is weighed, dissolved in 100 c.c. of water, and acidified with nitric acid. Silver nitrate solution is then added until, after heating and stirring, no further precipitate is produced. The precipitate is allowed to settle, the clear liquid decanted on a filter, and the precipitate then transferred and washed thoroughly with hot water. The precipitate and filter are then dried, the precipitate is transferred to a crucible, and the filter burned on the crucible lid. If an appreciable amount of the precipitate adheres to the filter, it is best to moisten the burned residue with a drop or two of nitro-hydrochloric acid, to reconvert any metallic silver, which may have been formed, into chloride. The small residue is then transferred to the crucible, the lid put on, and the whole heated in an air-bath to 130° until the weight is constant. The whole operation should be conducted as rapidly as possible, because silver chloride is decomposed by the light. The weight, after deducting that of crucible, lid, and ash, is silver chloride, AgCl, from which the percentage of chlorine found may be calculated.

Estimation of the Water.

Another portion, about 1 gramme, of the salt is weighed in a crucible or on a watch crystal, the salt and container placed in an air-bath at 120°, and maintained at that temperature until, on weighing at intervals of one-half hour, no further loss in weight occurs. The loss from the original weight represents the water.

COPPER SULPHATE, $CuSO_4.5H_2O$.

Estimation of the Copper.

About 0.400 gramme are weighed, dissolved in 25 to 50 c.c. of water in a porcelain dish, and boiled with a slight excess of potassium hydrate solution, until the cupric hydrate, which is first formed, is converted into black cupric oxide. The precipitate is washed two or three times by boiling with fresh portions of water, decanting each time ; it is then transferred to the filter and washed with hot water until the washings cease to change red litmus paper. The precipitate is dried, and when possible separated from the filter ; the latter is burned on the crucible lid, and the residue, after burning, is moistened with a drop or two of nitric acid, and again heated to reconvert into oxide any metallic copper that may have been formed by the reducing action of the burning paper. .This residue is then transferred to the crucible with the precipitate, and the whole ignited and weighed. The product is cupric oxide, CuO.

Estimation of the Sulphuric Acid.

Another portion of the salt is weighed, dissolved in water, and the sulphuric acid precipitated by the addition of barium chloride. The contents of the beaker are well boiled, and the precipitate of barium sulphate treated exactly as in the estimation of Barium.

Estimation of the Water.

The five molecules of water of crystallization in this salt are given off at a temperature of 200°. The estimation, therefore, is best accomplished by heating a weighed quantity of the salt in an air-bath at the above temperature until no further loss occurs.

POTASSIUM NITRATE, KNO_3.

Estimation of the Potassium.

A weighed quantity of the salt is dissolved in a little water, hydrochloric acid is added, and the mixture is carefully evaporated to dryness to remove nitric acid. The residue is dissolved in a small amount of water with a few drops of hydrochloric acid, and solution of platinic chloride is added in excess. The mixture is carefully evaporated nearly to dryness over a water-bath, keeping the water in the bath just below the boiling point. The residue is treated with 80 per cent. alcohol and allowed to stand some hours. The result is a complete conversion of the potassium into insoluble potassium platinic chloride, K_2PtCl_6. Two small filters are exactly balanced; one is placed inside the other, and the precipitate transferred to them. It is washed repeatedly with 80 per cent. alcohol. The filters and contents are then carefully dried, and finally heated in an air-bath to 130°. In weighing the precipitate, the outer filter is placed on the pan with the weights.

Estimation of the Nitric Acid.

Potassium nitrate is fused at as low a temperature as possible in a platinum crucible, and poured out on a porcelain slab to cool.

Three grammes of finely powdered silica are heated in a crucible, and, after cooling, weighed. One gramme of the finely powdered potassium nitrate is mixed with the silica in the crucible, and the mixture brought to a low red heat until the weight is constant. The loss indicates the amount of N_2O_5, and from this the amount of NO_3 which was present can be calculated. Sulphates and chlorides are not decomposed at this temperature.

MAGNESIUM SULPHATE, $MgSO_4.7H_2O$.

Estimation of the Magnesium.

To a weighed quantity of the salt, dissolved in water, solution of ammonium chloride is added in slight excess, then water of ammonia, until, after stirring, the mixture smells strongly of it. If the ammonia water produce a precipitate it is evidence that sufficient ammonium chloride has not been added. When the solution remains clear after the addition of the hydrate, sodium phosphate is added in excess, the mixture is stirred, without allowing the rod to touch the sides of the beaker, and then set aside for 24 hours without warming.

The clear, supernatant liquid is poured on a filter, and the precipitate then transferred to the same, using a little of the clear filtrate to wash the last portions on if necessary.

The precipitate is then washed with a mixture of 3 parts water and 1 part ammonia water, until a few drops of the washings, acidified with nitric acid, give no precipitate with silver nitrate.

The precipitate is then dried and transferred to a crucible, the filter burned separately, and the whole ignited strongly until the weight is constant. The residue consists of magnesium pyrophosphate, $Mg_2P_2O_7$.

Estimation of the Sulphuric Acid.

The sulphuric acid is estimated in another portion of the salt by precipitation with barium chloride in the presence of hydrochloric acid. The resulting barium sulphate is collected, washed, dried, ignited, and weighed as under Barium.

Estimation of the Water.

The water of crystallization is estimated in this salt by exposing a weighed quantity of it in a crucible to a low red heat until the weight becomes constant.

CALCIUM CARBONATE, $CaCO_3$.

Estimation of the Calcium.

A weighed quantity of the carbonate is dissolved in dilute hydrochloric acid, ammonium hydrate is added until the liquid is slightly alkaline, and then ammonium oxalate in slight excess, and the whole set aside for 24 hours. The clear, supernatant liquid is then decanted to a filter, the precipitate is washed once or twice by decantation, and then transferred to the filter and washed with several small portions of water, allowing each portion to completely drain through before adding more. The filter and precipitate are then dried and ignited. A good Bunsen burner is sufficient to effect the change into oxide provided the heat is continued sufficiently long. A blast lamp will accomplish the result more quickly. The heat in either case must be continued until no further loss in weight occurs. The residue is calcium oxide, CaO.

Estimation of the Carbonic Acid.

This, in some cases, is done by ignition, but the method adapted to nearly all cases is to treat the carbonate with dilute hydrochloric acid and estimate the loss as carbon dioxide. Any one of the numerous designs of apparatus offered by instrument makers may be employed, but that known as Schroetter's is probably the best.

FERROUS SULPHATE, $FeSO_4.7H_2O$.

Estimation of the Iron.

When iron is estimated gravimetrically it is weighed in the ferric state as ferric oxide, Fe_2O_3. For the estimation of ferrous iron volumetric processes are usually employed.

A weighed quantity of the salt is dissolved in water, a few drops of sulphuric acid added, and the mixture heated to the boiling point. Nitric acid is then dropped in until oxidation to ferric iron is effected, and then water of ammonia is added until the solution smells strongly of it after stirring. The precipitate of ferric hydrate is allowed to settle, and the clear, supernatant liquid poured on a filter. More water is added to the precipitate, and the mixture, after stirring again, allowed to settle; and, after pouring the clear liquid on the filter, the precipitate is transferred to the same, and washed thoroughly with hot water until the washings cease to have an alkaline reaction. The filter and precipitate are dried, ignited, and weighed, the residue being ferric oxide, Fe_2O_3.

Estimation of the Sulphuric Acid.

This is effected in exactly the same manner as described under Cupric Sulphate.

Estimation of the Water.

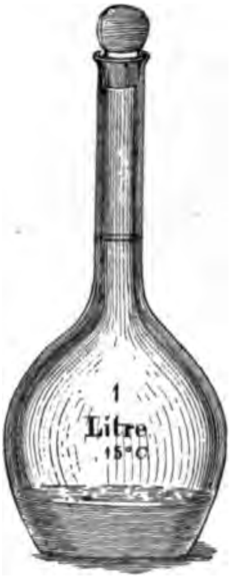
The water of crystallization in this salt is completely dissipated at 300°, and may be accomplished by carefully heating it over a gas flame to a temperature a little below redness. In case the above temperature is much exceeded, however, decomposition of the salt will take place; therefore the desired end may be reached by heating a weighed quantity of the salt in an air-bath to 115°, when all but one molecule of water will be driven off, leaving a residue of $FeSO_4.H_2O$. The loss should be six-sevenths of the total theoretical amount of water in the salt.

CHAPTER II.

VOLUMETRIC PROCESSES.

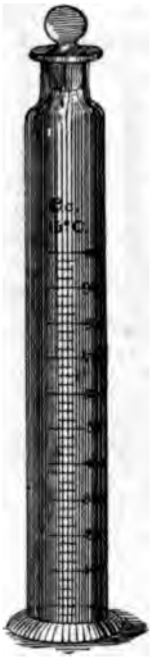
VOLUMETRIC analysis is the process of determining the amount of a substance by the use of a suitable reagent in a solution of known strength. These reagents in solution are known as *volumetric solutions*, and "are designated as normal ($\frac{N}{1}$) when they contain in 1 liter the molecular weight of the active reagent, expressed in grammes, and reduced to the valency corresponding to one atom of replaceable hydrogen or its equivalent."—U. S. P.

FIG. 112.



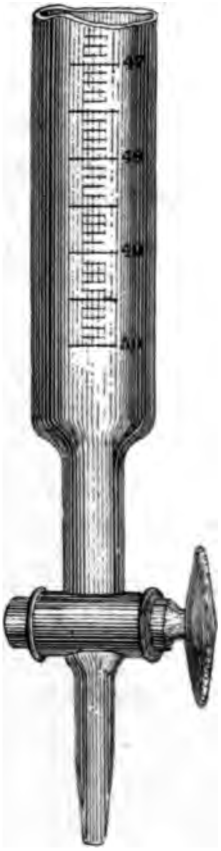
Liter flask.

FIG. 113.



Graduated cylinder.

FIG. 114.



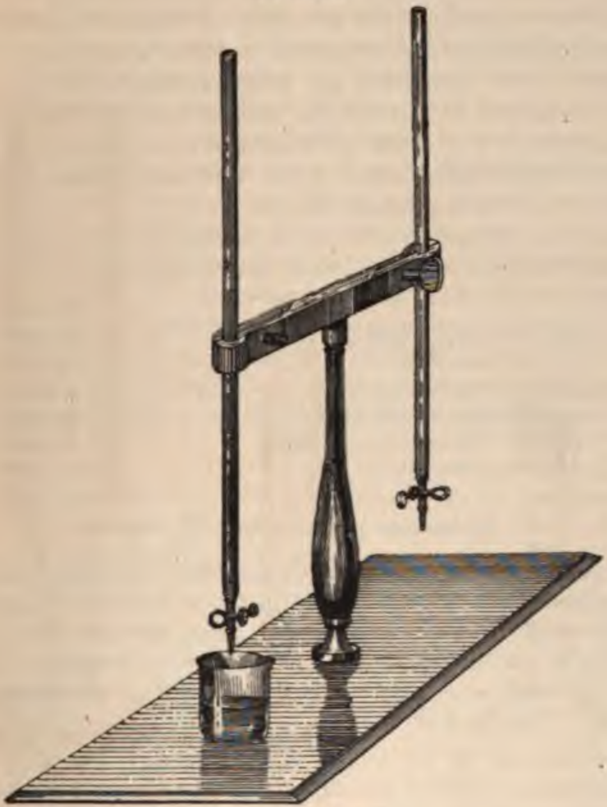
Geissler burette.

A decinormal solution ($\frac{N}{10}$) is one-tenth the strength of the normal one; and for many operations solutions of this strength are preferable.

The terms *acidimetry* and *alkalimetry* are applied to the processes of estimating acids and alkalies respectively by neutralization, and, therefore, usually by the employment of volumetric solutions.

The apparatus required for volumetric operations consists of a *liter flask* (Fig. 112), a 1000 c.c. *cylinder*, graduated (Fig. 113), *2 burettes* of 50 or 100 c.c. capacity, graduated to $\frac{1}{10}$ c.c.,—the form known as Geissler's (Fig. 114) is the most desirable,—a suitable *holder* (Fig. 115) for these, and a few *pipettes*, assorted sizes, some of which are graduated to $\frac{1}{10}$ c.c.

FIG. 115.



Burettes and holder.

Decinormal Oxalic Acid Volumetric Solution.

Containing 6.285 grammes, $H_2C_2O_4.2H_2O$, *in 1 liter.*

This solution is usually the starting point in the operations involving the estimation of acids and alkalies. Oxalic acid may be purchased in a pure state or can be purified by making a saturated solution of the acid in water, filtering and concentrating to three-fourths of its volume. The first crop of crystals is rejected as containing salts, and the second crop is preserved as pure. 6.285 grammes of the pure acid are weighed, transferred to a liter flask, about 500 c.c. of distilled water are added, and the crystals dissolved. The whole is brought to a temperature of about 15°, and with distilled water of the same temperature the solution is brought to the volume of 1 liter.

One cubic centimeter of this solution contains 0.006285 gramme of oxalic acid, and is equivalent to the following:

	Gramme.
Oxalic Acid, $H_2C_2O_4.2H_2O$	0.006285
Ammonia Gas, NH_3	0.001701
Calcium Hydrate, $Ca(OH)_2$	0.003691
Potassium Hydrate, KOH	0.005599
Potassium Permanganate, $KMnO_4$	0.0031534
Sodium Hydrate, NaOH	0.003996

Estimation of Potassium Hydrate.

The simplest estimation with the volumetric solution of oxalic acid is that of potassium hydrate. 0.500 to 1 gramme of the hydrate is weighed in a closely corked, clean, dry test-tube, rinsed out into a beaker containing 50 to 100 c.c. of water, and the resulting solution colored with a few drops of phenolphtalein solution. The beaker, with its contents, is set under a burette containing some of the oxalic acid solution. This solution is slowly run in, and the mixture constantly stirred with a glass rod until the red color just ceases to be visible. The proof of this is that one drop of a similar alkali solution will restore the red color.

If 0.500 gramme of potassium hydrate were used, and it were pure, it would be found that 89.3 c.c. of the oxalic solution had been used, but if we suppose that 85 c.c. were necessary, then, as every cubic centimeter of the oxalic acid solution is equal to 0.005599 gramme of potassium hydrate, we have $85 \times 0.005599 = 0.476$, the amount of potassium hydrate found. The following proportion will then yield the percentage of absolute potassium hydrate in the sample :

0.500 : 476 :: 100 : 95.20 per cent.

Decinormal Potassium Hydrate Volumetric Solution.

Containing 5.599 grammes of KOH *in 1 liter.*

As potassium hydrate is not obtainable, except it contains an unknown amount of water, it is necessary to standardize its solution. For this purpose about 7.5 grammes of the hydrate are taken, transferred to a graduated cylinder, and 1000 c.c. of distilled water added. 100 c.c. of decinormal solution of oxalic acid are placed in a beaker, a few drops of phenolphtalein solution added, and the alkaline solution added from a burette until the red color of the indicator just begins to appear.

If it has required 95 c.c. of the potassium hydrate solution to neutralize 100 c.c. of the oxalic acid solution, then it is evident that 950 c.c. of the former, when diluted to 1000, would have the same strength as the oxalic acid solution.

One cubic centimeter of this solution contains 0.005599 gramme of potassium hydrate, and is equivalent to the following :

	Gramme.
Potassium Hydrate, KOH	0.005599
Sodium Hydrate, NaOH	0.003996
Ammonia Gas, NH_3	0.001701
Ammonium Chloride, NH_4Cl	0.005338
Acetic Acid, absolute, $HC_2H_3O_2$	0.005986
Citric Acid, $H_3C_6H_5O_7.H_2O$	0.006983
Hydrobromic Acid, absolute, HBr	0.008076
Hydrochloric Acid, absolute, HCl	0.003637
Hydriodic Acid, absolute, HI	0.012753
Hypophosphorous Acid, HPH_2O_2	0.006588
Lactic Acid, absolute, $HC_3H_5O_3$	0.008979
Nitric Acid, absolute, HNO_3	0.006289
Oxalic Acid, crystallized, $H_2C_2O_4.2H_2O$	0.006285
Phosphoric Acid, H_3PO_4 (to form K_2HPO_4; with phenolphtalein)	0.004890
Phosphoric Acid, H_3PO_4 (to form KH_2PO_4; with methyl-orange)	0.009780
Potassium Dichromate, $K_2Cr_2O_7$	0.014689
Sulphuric Acid, absolute, H_2SO_4	0.004891
Tartaric Acid, crystallized, $H_2C_4H_4O_6$	0.007482

Decinormal Sulphuric Acid Volumetric Solution.

Containing 4.891 grammes of Sulphuric Acid in 1 liter.

About 3 c.c. of pure, concentrated sulphuric acid are poured carefully into 1000 c.c. of water, and the mixture allowed to cool. 100 c.c. of decinormal solution of potassium hydrate are placed in a beaker, a few drops of phenolphtalein solution are added, and sufficient of the sulphuric acid solution is run in to just destroy the color of the indicator. If 85 c.c. of the acid have been necessary, then 850 c.c. of the remainder of the acid solution should be diluted with water to 1000 c.c. Another trial should be made with the diluted solution to prove that it is exactly the strength of the potassium hydrate solution.

One c.c. of Decinormal Sulphuric Acid Solution contains 0.004891 gramme of H_2SO_4, and is the equivalent of:

	Gramme.
Potassium Hydrate, KOH	0.005599
Combined alkaloids of Nux Vomica, assumed to consist of equal parts of Strychnine and Brucine	0.0364

Decinormal sulphuric acid is preferable in many cases to oxalic acid solution of the same strength, and is equivalent to the same quantities of the substances given under the latter.

Decinormal Iodine Volumetric Solution.

Containing 12.653 grammes of Iodine in 1 liter.

12.653 grammes of pure iodine are weighed out in a closed test-tube or weighing-bottle, and transferred to a liter flask containing 18 grammes of potassium iodide in 200 c.c. of water. When solution of the iodine has been effected, water is added until the volume amounts to 1000 c.c. This solution should be kept in well-stopped containers in a cool place.

One c.c. of Decinormal Iodine Volumetric Solution is the equivalent of:

	Gramme.
Iodine	0.012653
Arsenic Trioxide, As_2O_3	0.004942
Potassium Sulphite, crystallized, $K_2SO_3.2H_2O$	0.009692
Sodium Bisulphite, $NaHSO_3$	0.005193
Sodium Hyposulphite (Thiosulphate), crystals, $Na_2S_2O_3.5H_2O$	0.024764
Sodium Sulphite, crystallized, $Na_2SO_3.7H_2O$	0.012579
Sulphur Dioxide, SO_2	0.003195
Antimony and Potassium Tartrate, crystals, $2K(SbO)C_4H_4O_6.H_2O$	0.016560

Decinormal Sodium Hyposulphite Volumetric Solution.

Containing 24.764 grammes of Sodium Thiosulphate in 1 liter.

32 grammes of the crystallized salt are dissolved in 1000 c.c. of water. 100 c.c. of the decinormal iodine solution are placed in a beaker, and the thiosulphate solution run in from a burette until the color of the iodine nearly disappears; a few drops of starch solution are then added, and then more of the thiosulphate, until the blue color is discharged.

The number of cubic centimeters of thiosulphate solution multiplied by 10 are diluted to 1000 c.c. Another trial should be made with the diluted solution to prove that it is of the same strength as the iodine solution.

The substances estimated by this solution either contain free iodine, or develop it on the addition of potassium iodide, so that starch solution is used as an indicator.

One c.c. of Decinormal Sodium Hyposulphite Solution is the equivalent of:

	Gramme.
Sodium Hyposulphite, $Na_2S_2O_3.5H_2O$	0.024764
Bromine, Br	0.007976
Chlorine, Cl	0.003537
Iodine, I	0.012653
Iron, Fe, in ferric salts	0.005588

Decinormal Potassium Dichromate Volumetric Solution.

Containing 4.896 grammes of Potassium Dichromate in 1 liter.

This solution is made by dissolving 4.896 grammes of the pure salt in about 500 c.c. of water in a liter flask, and then bringing the volume to 1000 c.c. When made of this strength, the solution is the equivalent of equal volumes of decinormal potassium permanganate solution, or, in the case of iodine liberated from potassium iodide, it is the equivalent of equal volumes of decinormal sodium hyposulphite solution.

In order to estimate iron in the ferrous state with this solution, the solution of the iron salt is acidified with sulphuric acid, and the dichromate solution run into it carefully, withdrawing a drop occasionally, and testing on a white porcelain surface with solution of potassium ferricyanide, until a green and not a blue color is obtained.

One c.c. of Decinormal Potassium Dichromate Solution is the equivalent of:

	Gramme.
Potassium Dichromate, $K_2Cr_2O_7$	0.0048963
Iron, in ferrous compounds	0.0055880
Ferrous Sulphate, anhydrous, $FeSO_4$	0.0151700
Ferrous Sulphate, crystallized, $FeSO_4.7H_2O$	0.0277420
Ferrous Sulphate, dried, $2FeSO_4.3H_2O$	0.0178640

Decinormal Potassium Permanganate Volumetric Solution.

Containing 3.1534 grammes of Potassium Permanganate in 1 liter.

This solution is prepared by standardizing it with decinormal solution of oxalic acid. For this purpose 3.5 grammes of the pure, crystallized permanganate are dissolved in 1000 c.c. of recently boiled and cooled distilled water. 10 c.c. of the decinormal oxalic acid solution are placed in a beaker, 1 c.c. of concentrated sulphuric acid added, and the solution of permanganate carefully added until a drop ceases to be decolorized after stirring, but imparts a pinkish tinge to the liquid. The number of c.c. of the permanganate solution used is multiplied by 100, and that number of c.c. of the liquid diluted to 1000 c.c. A trial should then be made to ascertain that 50 c.c. of the oxalic acid solution will destroy the color of exactly 50 c.c. of the permanganate solution.

This solution is liable to deteriorate on exposure or standing, and should be standardized with oxalic acid every few days.

The strength of the potassium permanganate solution is based on the weight of two molecules of the salt, 315.34.

With oxalic acid $2KMnO_4$ give off 5 atoms of oxygen to convert 5 molecules of the acid into water and carbon dioxide, as follows:

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

Three molecules of sulphuric acid are required to convert the potassium and manganese into sulphates.

With ferrous sulphate 5 atoms of oxygen are required to convert $10FeSO_4.7H_2O$ into $5Fe_2(SO_4)_3$ with the aid of $8H_2SO_4$, as follows:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$

With hydrogen dioxide the reaction is as follows:

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10O.$$

One c.c. of Decinormal Potassium Permanganate Solution is the equivalent of:

	Gramme.
Potassium Permanganate, $KMnO_4$	0.0031534
Barium Dioxide, BaO_2	0.008441
Iron, in ferrous compounds, Fe	0.005588
Ferrous Carbonate, $FeCO_3$	0.011573
Ferrous Sulphate, anhydrous, $FeSO_4$	0.015170
Ferrous Sulphate, crystals, $FeSO_4.7H_2O$	0.027742
Ferrous Sulphate, dried, $2FeSO_4.3H_2O$	0.017864
Hydrogen Dioxide, H_2O_2	0.001696
Hypophosphorous Acid, HPH_2O_2	0.001647
Oxalic Acid, crystallized, $H_2C_2O_4.2H_2O$	0.006285
Oxygen, O	0.000798

Decinormal Silver Nitrate Volumetric Solution.

Containing 16.955 grammes of Silver Nitrate in 1 liter.

This solution is prepared by dissolving 16.955 grammes of pure silver nitrate in sufficient water to make, at or near 15°, exactly 1000 c.c. The solution should be preserved in small, glass-stoppered vials, and light excluded.

The usual method of estimation with this solution is to add a few drops of potassium chromate solution to the solution of the salt under examination. On running in the silver nitrate solution from a burette, the first appearance of a permanent reddish precipitate of silver chromate is an indication of the end of the reaction. The use of an indicator may be dispensed with if sufficient care is exercised to detect when a precipitate ceases to form. This result is attained by allowing the precipitate to subside after each addition of a small quantity of the volumetric solution. Rapid stirring or agitation will aid in the separation of the precipitate, and in some cases it is also necessary to apply heat.

In the case of ferrous iodide, the addition of potassium chromate solution is inadmissible. With potassium cyanide or hydrocyanic acid the volumetric solution may be added, without the use of an indicator, until the formation of a permanent precipitate is observed; in which case just one-half the number of c.c. will be required as when the indicator is employed.

One c.c. of Decinormal Silver Nitrate Solution is the equivalent of:

	Gramme.
Silver Nitrate, $AgNO_3$	0.016955
Ammonium Bromide, NH_4Br	0.009777
Ammonium Chloride, NH_4Cl	0.005338
Ferrous Bromide, $FeBr_2$	0.010770
Ferrous Iodide, FeI_2	0.015447
Hydrocyanic Acid, absolute, HCN, with indicator	0.002698
Hydrocyanic Acid, absolute, HCN, to first formation of precipitate	0.005396
Hydriodic Acid, HI	0.012753
Hydrobromic Acid, HBr	0.008076
Potassium Bromide, KBr	0.011879
Potassium Iodide, KI	0.016556
Sodium Chloride, NaCl	0.005837

Alkaline Cupric Tartrate Volumetric Solution.

Fehling's Solution.

The directions as laid down in the U. S. Pharmacopœia are the best to follow in the preparation of this solution. They are as follows:

"A. *The Copper Solution.*—Dissolve 34.640 grammes of carefully selected, small crystals of pure cupric sulphate, showing no trace of efflorescence or of adhering moisture, in a sufficient quantity of water to make the solution measure, at or near 15°, exactly 500 c.c.

"Keep this solution in small, well-stoppered bottles.

"B. *The Rochelle Salt Solution.*—Dissolve 173 grammes of potassium and sodium tartrate and 125 grammes of potassium hydrate in a sufficient quantity of water to make the solution measure, at or near 15°, exactly 500 c.c.

"Keep the solution in small, rubber-stoppered bottles.

"For use, mix exactly equal volumes of the two solutions at the time required.

"One c.c. of the mixed solution is the equivalent of:

	Gramme.
Cupric Sulphate, crystallized, $CuSO_4.5H_2O$	0.03464
Cupric Tartrate, $CuC_4H_4O_6.3H_2O$	0.03685
Glucose, anhydrous, $C_6H_{12}O_6$	0.00500"

Fehling's solution is used in estimating glucose, by taking a solution of the latter in a burette and running it into a definite quantity of Fehling's solution, say 10 c.c., mixed with an equal volume of water, and heated to boiling in a porcelain capsule. The end of the reaction is known by the disappearance of the blue color.

Decinormal Mercuric Potassium Iodide Volumetric Solution.

MAYER'S SOLUTION.

Containing 39.200 grammes of Mercuric Potassium Iodide in 1 liter.

Mayer's solution is made by dissolving 13.546 grammes of pure mercuric chloride in 600 c.c. of water, and 49.8 grammes of pure potassium iodide in 100 c.c. of water. The two solutions are then mixed, and sufficient water is added to bring the volume to exactly 1000 c.c.

This solution is used in estimating a number of the alkaloids, as follows: A dilute solution of the alkaloid is distinctly acidified, placed in a beaker, and the volumetric Mayer's solution run in from a burette so long as a distinct precipitate is produced. The end of the reaction is determined by running a few drops of the mixture through a small filter, and a drop of the clear filtrate is brought on a piece of glass, on a black surface, with a drop of the reagent, when any cloudiness can be noted. Before the end of the reaction is finally reached all the portions taken out must be washed back into the beaker. The end of the reaction is known when the reagent produces no further precipitate, and yet is not in excess. The solution of the alkaloid must not contain much alcohol, and must not be acid with acetic acid. The compounds formed by Mayer's reagent with the different alkaloids vary somewhat. Some have the composition $BHI.HgI_2$, for example, strychnine; the compound with morphine is a mixture of $B(HI)_4.(HgI_2)_3$ and $B(HI)_6.(HgI_2)_3$; while with quinine it is not far from the composition $B_2(HI)_3.(HgI_2)_3$ (B represents the base, strychnine, morphine, or quinine). The amount of alkaloid present cannot be calculated from the formula, but has been determined experimentally for each one.*

At the present time the following equivalents are taken as the best that are known:

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* A full discussion of the compounds of this reagent with the alkaloids may be found in Prescott's " Manual of Organic Analysis."

One c.c. of the Decinormal Mercuric Potassium Iodide Solution is the equivalent of:

	Gramme.
Mercuric Potassium Iodide, $HgI_2.2KI$	0.0392
Aconitine	0.0269
Atropine in 5-per-cent. solution	0.0097
Hyoscyamine	0.00698
Coniine	0.0125
Nicotine	0.00405
Emetine	0.0189
Strychnine	0.0167
Brucine	0.0197
Morphine	0.020
Narcotine	0.0213
Veratrine	0.0296
Physostigmine	0.01375
Berberine	0.0425
Quinine	0.0108
Quinidine	0.0120
Cinchonine	0.0102

SECTION III.

PHARMACEUTICAL ASSAYING.

CHAPTER I.

ORGANIC DRUGS.

THE processes for the assay of a few of the most important drugs are given here in the belief that in them will be found all that is usually required by the pharmacist, and that where an assay is required of a new drug some one of these processes may be applicable to it.

Apparatus.—Such apparatus as has already been described in this work under gravimetric and volumetric operations is sufficient, except that occasionally an apparatus for continuous extraction will be found useful. One can choose any of the various forms of extraction apparatus offered by dealers, or he can readily construct one for himself if an upright condenser is at hand. For hot extraction the Soxhlet tube is about as satisfactory as any.

Solvents.—Ether, alcohol, and chloroform are the solvents usually employed; occasionally carbon disulphide, petroleum ether, and benzene will be found useful adjuncts to these. A mixture known as *Prollius' fluid*, and composed of 32.5 c.c. of ether, 2.5 c.c. of alcohol, and 1 c.c. of stronger ammonia water, is useful in extracting a number of drugs, and especially in the treatment of those whose composition is unknown.

General Process of Alkaloidal Assay.—With many drugs extraction of the active principle may be effected by the maceration of 10 grammes of the substance in fine powder with 100 c.c. of Prollius' fluid for 24 hours; 50 c.c. of the clear liquid are then withdrawn and evaporated until the ether is removed. The residual liquid is treated with 0.5 c.c. of dilute sulphuric acid and 10 c.c. of water and filtered into a separating funnel, the undissolved resinous substance and the filter being washed with about 5 c.c. more of water. The liquid in the separator is agitated with

2 or 3 portions of 10 c.c. each of ether to remove resin and coloring matter. After separation of the last portion of ether the aqueous solution is rendered alkaline with sodium hydrate, and shaken in the separating funnel with a mixture of 3 volumes of ether and 1 volume of chloroform; the ethereal portion is removed, and the aqueous solution shaken successively with two more portions of the mixture of ether and chloroform. The three ethereal solutions are mixed and evaporated to dryness in a tared beaker; any residue is weighed, then dissolved in very dilute acid, and its character established by the application of the numerous alkaloidal reagents; of these, Mayer's solution, as given under Volumetric Processes, may be applied either for qualitative or quantitative purposes.

Where the proportion of alkaloid in a drug is very small, it may be necessary to use larger quantities of the material for extraction, and alcohol of the specific gravity 0.820 is a useful and effective solvent. The alcohol is recovered by distillation, the residue poured into acidulated water, and treated as in the foregoing process.

Glucosides and other active principles are frequently removed from the acid solutions, obtained in the preceding processes, just before making them alkaline for removal of alkaloids, by agitation with one or more immiscible solvents, as petroleum ether, benzene, or chloroform. According to Dragendorff ("Plant Analysis," page 49), petroleum ether will remove from acid solution small quantities of *salicylic acid* and *piperin*; it will also remove *benzoic acid*. The same authority gives the following substances as removable from acid solution by benzene: *santonin*, *caryophyllin*, *cubebin*. *digitalin*, *cascarillin*, *elaterin*, *populin*, *colocynthin*, *quassin*, *ericolin*, *caffeine*, *piperin*, *colchiceine*, and *berberine*,—the last in small quantity only. He also gives the following list of principles removable from similar solutions by chloroform: *benzoic acid*, *saponin*, *senegin*, *æsculin*, *picrotoxin*, *helleborein*, *cinchonine*, *theobromine*, *papaverine*, *narceine*; it also removes the substances which are removable by petroleum ether and benzene. From alkaline solutions petroleum ether removes the following: *coniine*, *methyl coniine*, *nicotine*, *lobeliine*, *sparteine*, and small quantities of *strychnine*, *brucine*, *emetine*, *veratrine*, *sabadilline*, and *sabatrine*. Benzene removes, in addition to the above, *atropine*, *hyoscyamine*, *physostigmine*, *pilocarpine*, *gelsemine*, *quinidine*, *narcotine*, *codeine*, *thebaine*, *aconitine* and *cinchonine* (a trace). In addition to these, again, chlorofor extracts from alkaline solution *cinchonine*, *quinine*, *papaverine*, *narceine*, and small quantities of *morphine*.

Assay of Opium.

(*According to the U. S. Pharmacopœia of 1890.*)

Opium, in any condition to be valued, *ten grammes*	10 gm.
Ammonia Water, *three and five-tenths cubic centimeters* . .	3.5 c.c.
Alcohol,	
Ether,	
Water, each, *a sufficient quantity.*	

Introduce the Opium (which, if fresh, should be in very small pieces, and if dry, in very fine powder) into a bottle having a capacity of about 300 c.c., add 100 c.c. of water, cork it well, and agitate frequently during twelve hours. Then pour the whole as evenly as possible upon a wetted filter having a diameter of 12 cm., and, when the liquid has drained off, wash the residue with water, carefully dropped upon the edges of the filter and the contents, until 150 c.c. of filtrate are obtained.

Then carefully transfer the moist Opium back to the bottle by means of a spatula, add 50 c.c. of water, agitate thoroughly and repeatedly during fifteen minutes, and return the whole to the filter.

When the liquid has drained off, wash the residue, as before, until the second filtrate measures 150 c.c., and finally collect about 20 c.c. more of a third filtrate. Evaporate in a tared capsule, first, the second filtrate to a small volume, then add the first filtrate, rinsing the vessel with the third filtrate, and continue the evaporation until the residue weighs 14 gm. Rotate the concentrated solution about in the capsule until the rings of extract are redissolved, pour the liquid into a tared Erlenmeyer flask having a capacity of about 100 c.c., and rinse the capsule with a few drops of water at a time, until the entire solution weighs 20 gm. Then add 10 gm. (or 12.2 c.c.) of alcohol, shake well, add 25 c.c. of ether, and shake again. Now add the ammonia water from a graduated pipette or burette, stopper the flask with a sound cork, shake it thoroughly during ten minutes, and then set it aside, in a moderately cool place, for at least six hours, or overnight.

Remove the stopper carefully, and, should any crystals adhere to it, brush them into the flask. Place in a small funnel two rapidly-acting filters, of a diameter of 7 cm., plainly folded, one within the other (the triple fold of the inner filter being laid against the single side of the outer filter), wet them well with ether, and decant the ethereal solution as completely as possible upon the inner filter. Add 10 c.c. of ether to the contents of the flask, rotate it, and again decant the ethereal layer upon the inner filter. Repeat this operation with another portion of 10 c.c. of ether. Then pour into the filter the liquid in the flask, in portions, in such a way as to transfer the greater portion of the crystals to the filter, and, when this has passed through, transfer the remaining crystals to the filter by washing the flask with several portions of water, using not more than about 10 c.c. in all. Allow the double filter to drain, then apply water to the crystals, drop by drop, until they are practically free from mother-water, and afterwards wash them, drop by drop, from a pipette, with alcohol previously saturated with powdered morphine.

When this has passed through, displace the remaining alcohol by ether, using about 10 c.c., or more if necessary. Allow the filter to dry in a moderately warm place, at a temperature not exceeding 60° C. (140° F.), until its weight remains constant, then carefully transfer the crystals to a tared watch-glass and weigh them.

The weight found in grammes, multiplied by 10, represents the percentage of crystallized morphine obtained from the Opium.

Assay of Opium.

(*According to the U. S. Pharmacopœia of 1880.*)

Opium, in any condition to be valued	7 grammes.
Lime, freshly slaked	3 grammes.
Chloride of Ammonium	3 grammes.
Alcohol,	
Stronger Ether,	
Distilled Water, each, *a sufficient quantity.*	

Triturate together the Opium, Lime, and 20 c.c. of Distilled Water, in a mortar, until a uniform mixture results; then add 50 c.c. of Distilled Water, and stir occasionally, during half an hour. Filter the mixture through a plaited filter, three to three and one-half inches (75 to 90 mm.) in diameter, into a wide-mouthed bottle or stoppered flask (having the capacity of about 120 c.c. and marked at exactly 50 c.c.), until the filtrate reaches this mark.

To the filtered liquid (representing 5 grammes of opium) add 5 c.c. of Alcohol and 25 c.c. of Stronger Ether, and shake the mixture; then add the Chloride of Ammonium, shake well and frequently during half an hour, and set it aside for twelve hours.

Counterbalance two small filters, place one within the other in a small funnel, and decant the ethereal layer as completely as practicable upon the filter. Add 10 c.c. of Stronger Ether to the contents of the bottle and rotate it; again decant the ethereal layer upon the filter, and afterwards wash the latter with 5 c.c. of Stronger Ether, added slowly and in portions. Now let the filter dry in the air, and pour upon it the liquid in the bottle, in portions, in such a way as to transfer the greater portion of the crystals to the filter. Wash the bottle, and transfer the remaining crystals to the filter, with several small portions of Distilled Water, using not much more than 10 c.c. in all, and distributing the portions evenly upon the filter. Allow the filter to drain, and dry it, first by pressing it between sheets of bibulous paper, and afterwards at a temperature between 55° and 60° C. (131° to 140° F.). Weigh the crystals in the inner filter, counterbalancing by the outer filter. The weight of the crystals in grammes, multiplied by *twenty*, equals the percentage of morphine in the Opium taken.

Assay of Tincture of Opium.

(According to the U. S. Pharmacopœia of 1890.)

Tincture of Opium, *one hundred cubic centimeters*	100 c.c.
Ammonia Water, *three and five-tenths cubic centimeters*	3.5 c.c.
Alcohol,	
Ether,	
Water, each, *a sufficient quantity.*	

Evaporate the Tincture to about 20 c.c., add 40 c.c. of water, mix thoroughly, and set the liquid aside for an hour, occasionally stirring, and disintegrating the resinous flakes adhering to the capsule. Then filter, and wash the filter and residue with water, until all soluble matters are extracted, collecting the washings separately. Evaporate in a tared capsule, first, the washings to a small volume, then add the first filtrate, and evaporate the whole to a weight of 14 gm. From this point proceed as directed in the case of the residue of the same weight in the Assay of Opium.

When Tincture of Deodorized Opium is to be assayed, the foregoing process and quantities are to be used.

When Vinegar of Opium is to be assayed, proceed as follows : Render 100 c.c. of the sample alkaline with ammonia water, add 2 c.c. of ether, shake vigorously for 10 minutes, and set aside for 6 hours or overnight. Collect the alkaloids upon a filter previously wetted with water, and wash them with a small quantity of water. Transfer the still moist precipitate to a small capsule, add 10 c.c. of 5-per-cent. sulphuric acid, or enough to impart acidity, warm on the water-bath, cool, allow to stand for an hour or more, filter, and wash the filter and residue well with water. Mix the filtrate and washings, add 10 gm. of alcohol, shake, add 25 c.c. of ether, shake again, and, commencing with the addition of ammonia water until the solution is alkaline, follow the directions from a corresponding point given in the assay of opium.

Assay of Cinchona.

(According to the U. S. Pharmacopœia of 1890.)

I.—FOR TOTAL ALKALOIDS.

Cinchona, in No. 80 (or finer) powder, and completely dried at 100° C. (212° F.), *twenty grammes*	20 gm.
Alcohol,	
Ammonia Water,	
Chloroform,	
Ether,	
Normal Sulphuric Acid V. S.,	
Normal Potassium Hydrate V. S., each, *a sufficient quantity.*	

To 20 gm. of Cinchona, in very fine powder, and contained in a bottle provided with an accurately ground glass stopper, add 200 c.c. of a previously prepared mixture of 19 volumes of alcohol, 5 volumes of chloroform, and 1 volume of ammonia water, stopper the bottle and shake it thoroughly and frequently during four hours. Then separate the liquid by pouring it into another bottle through a funnel containing a pellet of cotton, in such a manner that no material loss by evaporation may result.

Transfer 100 c.c. of the clear filtrate (representing 10 gm. of Cinchona) to a beaker, and evaporate it to dryness.

Dissolve the residue of crude alkaloids thus obtained in 10 c.c. of water and 4 c.c. of normal sulphuric acid V. S., with the aid of a gentle heat, filter the cooled solution into a separatory funnel, and wash the beaker and filter until the filtrate no longer has an acid reaction, using as small a quantity of water as possible.

Now add 5 c.c. of normal potassium hydrate V. S., or such an amount as will render the liquid decidedly alkaline, and extract the alkaloids by shaking the mixture, first with 20 c.c., and then repeatedly with 10 c.c., of chloroform, until a drop of the last chloroform extraction, when evaporated on a watch-glass, no longer leaves a residue. Evaporate the united chloroformic extracts in a tared beaker, dry the residue at 100° C. (212° F.), and weigh. The weight found in grammes, multiplied by *ten* (10), will give the percentage of *total alkaloids* in the specimen of Cinchona tested.

II.—FOR QUININE.

Transfer 50 c.c. of the clear filtrate remaining over from the preceding process (and representing 5 gm. of Cinchona) to a beaker, evaporate it to dryness, and proceed as directed in the assay for total alkaloids, using, however, only one-half the amounts of volumetric acid and alkali there directed. Add the united chloroformic extracts containing the alkaloids in solution, gradually, and in small portions at a time, to about 5 gm. of powdered glass contained in a porcelain capsule placed over a water-bath, so that, when the contents of the capsule are dry, all or nearly all of the dry alkaloids shall be in intimate admixture with the powdered glass, and the chloroform be completely expelled.

Now moisten the residue with ether, and, having placed a funnel containing a filter of a diameter of 7 cm., and well wetted with ether, over a small graduated tube (A), transfer to the filter the ether-moistened residue from the capsule. Rinse the latter several times, if necessary, with fresh ether, so as to transfer the whole of the residue to the filter, then percolate with ether added drop by drop, until exactly 10 c.c. of percolate have been obtained. Then collect another volume of 10 c.c., by similar, slow percolation with ether, in a second graduated tube (B). Transfer the contents of the two tubes completely (using ether for washing) to two small, tared capsules, properly marked (A and B) so as to avoid confusion, evaporate to a constant weight at 100° C. (212° F.), and weigh them.

(The residue in A will contain practically all the quinine, together with a portion of the alkaloids less soluble in ether; the residue in B will consist almost entirely of these alkaloids.) From the amount of residue obtained in capsule A deduct that contained in B, and multiply the remainder by *twenty* (20). The product will represent, approximately, the percentage of *quinine* (containing 1 molecule of water) in the specimen of Cinchona tested.

Assay of Extract of Nux Vomica.

(*According to the U. S. Pharmacopœia of 1890.*)

Extract of Nux Vomica, dried at 100° C. (212° F.), *two grammes* . 2 gm.
Alcohol,
Ammonia Water,
Water,
Chloroform,
Decinormal Sulphuric Acid V. S.,
Centinormal Potassium Hydrate V. S., each, *a sufficient quantity.*

Put 2 gm. of the dried Extract of Nux Vomica into a glass separator, add to it 20 c.c. of a previously prepared mixture of 2 volumes of alcohol, 1 volume of ammonia water (specific gravity 0.960), and 1 volume of water, and shake the well-stoppered separator until the extract is dissolved. Then add 20 c.c. of chloroform and agitate during five minutes. Allow the chloroform to separate, remove it as far as possible, pour into the separator a few c.c. of chloroform, and, without shaking, draw this off through the stop-cock to wash the outlet-tube. Repeat the extraction with two further portions of chloroform of 15 c.c. each, and wash the outlet-tube each time as just directed. Collect all the chloroformic solutions in a wide beaker, expose the latter to a gentle heat, on a water-bath, until the chloroform and ammonia are completely dissipated, add to the residue 10 c.c. of decinormal sulphuric acid measured with great care from a burette, stir gently, and then add 20 c.c. of hot water. When solution has taken place, add 2 c.c. of brazil wood T.S., and then carefully run in centinormal potassium hydrate V.S., until a permanent pinkish color is produced by the action of a slight excess of alkali upon the brazil wood indicator. Divide the number of c.c. of centinormal potassium hydrate V. S. used by 10, subtract the number found from 10 (the 10 c.c. of decinormal acid used), multiply the remainder by 0.0364, and that product by 50 (or, multiply at once by 1.82), which will give the percentage of *total alkaloids* in the Extract of Nux Vomica, it being assumed that strychnine and brucine are present in equal proportion, and the above factor being found by taking the mean of their respective molecular weights rounded off to whole numbers $[(334 + 394) \div 2 = 364]$.

When Tincture of Nux Vomica is to be assayed, 100 c.c. of it (representing 2 gm. of extract) should be evaporated to dryness, and the residue tested by the foregoing process.

Assay of Aconite.

(*According to A. B. Lyons.*)

The powdered root or leaves may be used in this process. 10 grammes are placed in a suitable flask, and 100 c.c. of Prollius' fluid added. After some agitation, the whole is set aside for 12 to 24 hours. 50 c.c. of the clear liquid are then removed with a pipette, and placed in a beaker with 5 c.c. of water. The ether is allowed to evaporate spontaneously, and, when nearly all has disappeared, 6 drops of 5-per-cent. sulphuric acid are added, and 10 c.c. of fresh ether. Thorough stirring is required at this time to insure complete solution of the alkaloid in the acid. The evaporation is then continued until all ether and alcohol have been removed. The volume of the liquid is then made up to 4 c.c. with water, and titrated with Mayer's reagent. Each cubic centimeter of the decinormal solution represents [illegible] gramme of [illegible], or, according to Dr. Lyons, 0.0190 gramme. It is therefore more exact to weigh the alkaloid, which may be accomplished by taking 50 c.c. from the flask containing the drug and Prollius', after maceration for 24 hours, and agitating in a separating funnel with 3 successive portions of 5 c.c. each, of water acidified distinctly with hydrochloric acid. The mixed acid solutions are placed in a separating funnel, washed once with 10 c.c. of ether, to remove the last traces of impurities, the ether is separated, and the acid solution, after returning to the separating funnel, is rendered alkaline with ammonia water, and agitated with two portions of ether of 20 c.c. each. The mixed ethereal washings are evaporated on a water-bath to constant weight; the result being the weight of alkaloid in 5 grammes of the drug.

Assay of Belladonna Root.

Of the numerous processes suggested for the analysis of this drug, that of Dunstan and Ransom, with some slight modifications, will probably be found the most satisfactory. 20 grammes of the finely powdered root are exhausted by hot percolation with a mixture of equal volumes of absolute alcohol and chloroform; about 60 c.c. of the mixture will be required. When exhaustion of the drug is complete, the liquid is transferred to a separator and agitated with two successive portions, of 20 c.c. each, of water acidified with a few drops of dilute sulphuric acid. The mixed acid solutions are washed in a separator with 10 c.c. of chloroform, to remove last traces of impurities, then rendered alkaline with ammonia water, and the alkaloid removed by two successive treatments with chloroform of 20 c.c. each. The mixed chloroformic solutions are washed with a little water, transferred to a tared beaker, and evaporated on a water-bath to constant weight.

Belladonna Leaves are assayed similarly to the root, using for extraction absolute alcohol, instead of a mixture of that liquid with chloroform.

Assay of Coca.

(*According to A. B. Lyons.*)

In a flask having a capacity of 120 c.c. are placed 10 grammes of the drug in moderately fine powder, 95 c.c. of ether, and 5 c.c. of a mixture of 19 volumes of absolute alcohol and 1 c.c. of stronger ammonia water. The whole is then set aside for 24 hours, with occasional agitation. 50 c.c. are then decanted, and, if not perfectly clear, filtered, the filter being washed with a little ether. The ethereal liquid is transferred to a separator containing 5 c.c. of water and 10 drops of diluted sulphuric acid. After thorough agitation, the acid solution is drawn off, and the ether in the separator is agitated successively with two more portions of acid water, of 3 c.c. each. The mixed acid solutions are transferred to a separator, washed with 15 c.c. of ether, and the latter removed. Water of ammonia is then added to the acid solution in the separator until the mixture becomes decidedly alkaline, and the alkaloid is removed by agitation of this alkaline liquid with at least three successive portions of ether of 15 c.c. each. The mixed ethereal liquids are evaporated, in a tared beaker, to constant weight on a water-bath.

Assay of Ipecac.

(*According to C. C. Keller.*)

10 grammes of the powdered drug are placed in a funnel, closed with a plug of cotton, and percolated with 20 to 25 c.c. of ether, to remove fat. The dried powder is then transferred to a flask of 150 c.c. capacity, 60 c.c. of ether and 25 c.c. of chloroform are added, and the whole thoroughly mixed by agitation for some minutes. 10 c.c. of ammonia water are then added, by which means the suspended powder separates, while the emetine dissolves. Agitation is continued at frequent intervals for one hour, when 5 c.c. more of ammonia water are added, which causes the powder to still further agglutinate, while the liquid becomes clear. 50 c.c. of the clear liquid are removed to a weighed Erlenmeyer flask, the solvent is distilled off, and the varnish-like residue is washed with two portions of ether, of 5 c.c. each, and dried by forcing a gentle current of air through the flask. The residue, when weighed, gives the amount of emetine in 5 grammes. These results are usually rather high, and it is considered more exact to dissolve the residue in 10 c.c. of absolute alcohol, add 2 drops of hæmatoxylin solution, and titrate with decinormal hydrochloric acid solution until the violet-red color is changed to pale yellow. Each c.c. of acid used represents 0.0254 gramme of emetine.

Assay of Tea.

(*According to E. R. Squibb.*)

10 grammes of coarsely-powdered tea are intimately mixed in a mortar with 2 grammes of magnesium oxide. The mixture is added to 100 c.c. of boiling water, and the heat maintained at that temperature for 5 minutes. It is then poured on a filter and the residue washed with 50 c.c. of water, after which it is again stirred into 100 c.c. of boiling water. After boiling for a few minutes the mixture is filtered and the residue percolated with water until exhausted, using about 100 c.c., or making a total of about 350 c.c. of percolate. The weaker portion is evaporated first, the stronger added, and the whole concentrated to 20 c.c. The concentrated solution is transferred to a separator with a few c.c. of water, and washed successively with three portions of chloroform of 20 c.c. each. The mixed chloroformic washings are concentrated in a tared beaker, on a water-bath, to constant weight.

Assay of Coffee.

(According to E. R. Squibb.)

The same process is employed in coffee as in tea, using a finer powder, until the final 20 c.c. of aqueous solution are obtained. Instead of attempting to wash out the alkaloid from this solution with chloroform, it is poured into 100 c.c. of alcohol to precipitate albuminous matter. The mixture is filtered, the precipitate washed with alcohol, and the filtrate and washings concentrated on a water-bath to 20 c.c.; after which it is washed with three successive portions of chloroform of 20 c.c. each, and the mixed chloroformic solutions concentrated in a beaker, on a water-bath, to constant weight.

The Estimation of Nitrogen.

As it is sometimes desirable to estimate the nitrogen in alkaloids as well as other substances, the following methods are here given:

SODA-LIME METHOD.

This method of estimating nitrogen in organic substances is applicable in all cases in which that element does not exist as a nitrate. The adaptability of the process lies in the fact that nitrogenous organic substances, when strongly heated with an alkali hydrate, evolve their nitrogen as ammonia. The latter is absorbed in standard oxalic or sulphuric acid solution. The percentage of nitrogen is calculated from the amount of gas evolved. This is determined by titrating the known volume of standard acid with standard alkali.

The analysis is conducted by mixing the substance to be estimated with soda-lime (a granulated mixture of sodium hydrate and calcium oxide) and heating the mixture in a combustion-tube, some unmixed soda-lime being placed at both ends of the column of the mixture, and the whole held secure by plugs of asbestos.

The tube is placed in a combustion-furnace, and heated to redness a few inches back of the anterior end, to which a Varrentrapp and Will's absorption bulb, containing a convenient quantity of the standard acid, has been attached. The heat is then gradually extended along the tube to the posterior end. When absorption is no longer noticeable, this end is broken off and air drawn through the tube by suction applied to the absorption bulb. By the last treatment all traces of ammonia are absorbed.

Liquid nitrogenous compounds are weighed in small, sealed, glass bulbs, which are to be placed in a layer of soda-lime.

If the substance is rich in nitrogen some cane-sugar should be mixed with it.

THE KJELDAHL METHOD.

This method, which has largely superseded the soda-lime process for the estimation of nitrogen, is founded on the complete oxidation of organic substances when they are digested with concentrated sulphuric acid and potassium permanganate. The nitrogen is converted into ammonia, which at once combines with the excess of acid.

The following outline of the plan of application is taken from the Official Methods of Analysis adopted by the Association of Official Agricultural Chemists at its meeting in August, 1894. .7 to 3.5 gm. of the substance to be analyzed (according as the amount of nitrogen is likely to be much or little) are brought into a flask with an equal weight of yellow mercuric oxide, which hastens the oxidation, and 20 c.c. of sulphuric acid (sp. gr. 1.84). The mixture is then heated below the boiling point of the acid for from 5 to 10 minutes, or until frothing has ceased; to stop excessive frothing a small piece of paraffin may be added.

The heat is now increased until the acid boils, and the contents of the flask have become clear and colorless, or nearly so. Powdered potassium permanganate is now dropped in carefully and in small quantities at a time until, after shaking, the liquid remains of a green or purple color. After cooling, 200 c.c. of water are added. To prevent bumping during distillation a few pieces of granulated zinc are introduced into the flask, to the contents of which 1 gm. of potassium sulphide in solution is added with the view of obviating the formation of mercuro-ammonium compounds. 50 c.c. of saturated solution of sodium hydrate, or sufficient to make the mixture alkaline, are next added by pouring the same down the side of the flask so that it does not mix at once with the acid solution. The flask is then connected with a condenser, one end of which is inserted into another flask containing standard acid.

The contents of the distilling flask are now mixed by shaking, and distilled until all ammonia has passed over into the standard acid. The first 150 c.c. of the distillate will generally contain all the ammonia. The contents of the receiving flask are then titrated with standard alkali, cochineal test-solution being used as an indicator. The result is calculated from the amount of acid neutralized by the distillate.

The reagents and apparatus should be tested by a blank experiment with some non-nitrogenous substance, such, for instance, as sugar.

The foregoing treatment does not effect the estimation of nitrogen when the latter is present as nitrates.

To include the nitrogen of these compounds, the method may be modified as follows:

.7 to 3.5 gm. of the substance are well mixed with 30 c.c. of sulphuric acid (sp. gr. 1.84) and 1 gm. of salicylic acid; 5 gm. of crystallized sodium thiosulphate are then added. The last two substances may be replaced by 2 gm. of salicylic acid and 2 gm. of zinc-dust. The flask is heated over a low flame until all danger from frothing has passed; then the heat is raised until the mixture boils briskly, and continued until white fumes no longer pour out of the flask. This requires about 5 or 10 minutes.

A quantity of yellow mercuric oxide equal to the substance taken is now added, and the boiling continued until the liquid in the flask is colorless, or nearly so.

Additional acid may be supplied should the contents of the flask show indications of becoming solid.

Complete the oxidation with potassium permanganate in the usual way, and from this point proceed according to the regular method.

Since the institution of the Kjeldahl method, many variations in the details of the process have been suggested with the view of shortening the time of digestion with the sulphuric acid. Prominent among those that have thus far met with general approval is

THE GUNNING METHOD.

This differs from that of Kjeldahl in the replacement of the yellow mercuric oxide by 10 grammes of powdered potassium sulphate added in portions to the first mixture of the substance to be estimated and the usual amount of sulphuric acid. The boiling point of the acid is raised by this addition, and the oxidation of the organic matter thereby rendered complete without the aid of potassium permanganate, which is consequently dispensed with.

By omitting the mercuric oxide the use of potassium sulphide also becomes unnecessary.

The liberation of the ammonia, the distillation, and the titration are conducted as in the Kjeldahl method.

APPENDIX.

TABLE OF ATOMIC WEIGHTS ACCORDING TO THE U. S. PHARMACOPŒIA, TOGETHER WITH VALENCES.

NAME.	Symbol.	Atomic Weight.	Valence.
Aluminum	Al	**27.04**	III or $(Al_2)^{VI}$
Antimony	Sb	**119.6**	III, V
Arsenic	As	**74.9**	III, V
Barium	Ba	**136.9**	II, IV
Beryllium *	Be	**9.03**	II
Bismuth	Bi	**208.9**	III, V
Boron	B	**10.9**	III
Bromine	Br	**79.76**	I, III, V, VII
Cadmium	Cd	**111.5**	II
Cæsium	Cs	**132.7**	I
Calcium	Ca	**39.91**	II, IV
Carbon	C	**11.97**	IV
Cerium	Ce	**139.9**	$(Ce_2)^{VI}$, IV
Chlorine	Cl	**35.37**	I, III, V, VII
Chromium	Cr	**52.0**	II, $(Cr_2)^{VI}$, VI
Cobalt	Co	**58.6**	II, $(Co_2)^{VI}$
Columbium †	Cb	**93.7**	III, V
Copper	Cu	**63.18**	$(Cu_2)^{II}$, II
Didymium ‡	Di	**142.0**	III, V
Erbium	Er	**166.0**	III or $(Er_2)^{VI}$
Fluorine	F	**19.0**	I
Gallium	Ga	**69.9**	$(Ga_2)^{VI}$
Germanium	Ge	**72.3**	II, IV
Gold	Au	**196.7**	I, III
Hydrogen	H	**1.0**	I
Indium	In	**113.6**	III or $(In_2)^{VI}$
Iodine	I	**126.53**	I, III, V, VII
Iridium	Ir	**192.5**	II, IV
Iron	Fe	**55.88**	II, $(Fe_2)^{VI}$, VI
Lanthanum	La	**138.2**	III
Lead	Pb	**206.4**	II, IV
Lithium	Li	**7.01**	I
Magnesium	Mg	**24.3**	II
Manganese	Mn	**54.8**	II, IV, VI, VIII
Mercury	Hg	**199.8**	$(Hg_2)^{II}$, II
Molybdenum	Mo	**95.9**	II, IV, VI
Nickel	Ni	**58.6**	II, $(Ni_2)^{VI}$
Nitrogen	N	**14.01**	I, III, V
Osmium	Os	**190.3**	II, IV, VI, VIII

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* Also called Glucinum, Gl = 9.03.

† Also called Niobium, Nb = 93.7.

‡ Composed of Neo- and Praseo-Didymium.

TABLE OF ATOMIC WEIGHTS ACCORDING TO THE U. S. PHARMACOPŒIA, TOGETHER WITH VALENCES.—(*Continued.*)

NAME.	Symbol.	Atomic Weight.	Valence.
Oxygen	O	**15.96**	II
Palladium	Pd	**106.35**	II, IV
Phosphorus	P	**30.96**	III, V
Platinum	Pt	**194.3**	II, IV
Potassium	K	**39.03**	I
Rhodium	Rh	**102.9**	II, IV
Rubidium	Rb	**85.2**	I
Ruthenium	Ru	**101.4**	II, IV, VI, VIII
Samarium	Sm	**149.62**	III, V
Scandium	Sc	**43.97**	III or (Sc$_2$)$^{\text{vi}}$
Selenium	Se	**78.87**	II, IV, VI
Silicon	Si	**28.3**	IV
Silver	Ag	**107.66**	I
Sodium	Na	**23.0**	I
Strontium	Sr	**87.3**	II, IV
Sulphur	S	**31.98**	II, IV, VI
Tantalum	Ta	**182.0**	III, V
Tellurium	Te	**125.0**	II, IV, VI
Terbium	Tb	**159.1**	III
Thallium	Tl	**203.7**	I, III
Thorium	Th	**231.9**	IV
Tin	Sn	**118.8**	II, IV
Titanium	Ti	**48.0**	IV
Tungsten	W	**183.6**	II, IV, VI
Uranium	U	**238.8**	II, IV, VI
Vanadium	V	**51.1**	III, V
Ytterbium	Yb	**172.6**	III
Yttrium	Yt	**88.9**	III
Zinc	Zn	**65.1**	II
Zirconium	Zr	**90.4**	IV

THERMOMETRIC EQUIVALENTS.

(According to the Centigrade and Fahrenheit Scales.)

C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°
—39.4	—39	—20.5	—5	—1.1	30	18	64.4	37.2	99
—39	—38.2	—20	—4	—1	30.2	18.3	65	37.7	100
—38.8	—38	—19.4	—3	—0.5	31	18.8	66	38	100.4
—38.3	—37	—19	—2.2	0	32	19	66.2	38.3	101
—38	—36.4	—18.8	—2	0.5	33	19.4	67	38.8	102
—37.7	—36	—18.3	—1	1	33.8	20	68	39	102.2
—37.2	—35	—18	—0.4	1.1	34	20.5	69	39.4	103
—37	—34.6	—17.7	0	1.6	35	21	69.8	40	104
—36.6	—34	—17.2	1	2	35.6	21.1	70	40.5	105
—36.1	—33	—17	1.4	2.2	36	21.6	71	41	105.8
—36	—32.8	—16.6	2	2.7	37	22	71.6	41.1	106
—35 5	—32	—16.1	3	3	37.4	22.2	72	41.6	107
—35	—31	—16	3.2	3.3	38	22.7	73	42	107.6
—34.4	—30	—15.5	4	3.8	39	23	73.4	42.2	108
—34	—29.2	—15	5	4	39.2	23.3	74	42.7	109
—33.8	—29	—14.4	6	4.4	40	23.8	75	43	109.4
—33.3	—28	—14	6.8	5	41	24	75.2	43.3	110
—33	—27.4	—13.8	7	5.5	42	24.4	76	43.8	111
—32 7	—27	—13.3	8	6	42.8	25	77	44	111.2
—32.2	—26	—13	8.6	6.1	43	25.5	78	44.4	112
—32	—25.6	—12.7	9	6.6	44	26	78.8	45	113
—31.6	—25	—12.2	10	7	44.6	26.1	79	45 5	114
—31.1	—24	—12	10.4	7.2	45	26.6	80	46	114.8
—31	—23.8	—11.6	11	7.7	46	27	80.6	46.1	115
—30.5	—23	—11.1	12	8	46.4	27.2	81	46.6	116
—30	—22	—11	12.2	8.3	47	27.7	82	47	116.6
—29.4	—21	—10.5	13	8.8	48	28	82.4	47.2	117
—29	—20.2	—10	14	9	48.2	28.3	83	47.7	118
—28.8	—20	—9.4	15	9.4	49	28.8	84	48	118.4
—28.3	—19	—9	15.8	10	50	29	84.2	48.3	119
—28	—18.4	—8.8	16	10.5	51	29.4	85	48.8	120
—27.7	—18	—8.3	17	11	51.8	30	86	49	120.2
—27.2	—17	—8	17.6	11.1	52	30.5	87	49.4	121
—27	—16.6	—7.7	18	11.6	53	31	87.8	50	122
—26.6	—16	—7.2	19	12	53.6	31.1	88	50.5	123
—26.1	—15	—7	19.4	12.2	54	31.6	89	51	123.8
—26	—14.8	—6.6	20	12.7	55	32	89.6	51.1	124
—25.5	—14	—6.1	21	13	55.4	32.2	90	51.6	125
—25	—13	—6	21.2	13.3	56	32.7	91	52	125.6
—24.4	—12	—5.5	22	13.8	57	33	91.4	52.2	126
—24	—11.2	—5	23	14	57.2	33.3	92	52.7	127
—23 8	—11	—4.4	24	14.4	58	33.8	93	53	127.4
—23.3	—10	—4	24.8	15	59	34	93.2	53.3	128
—23	—9.4	—3.8	25	15.5	60	34.4	94	53.8	129
—22.7	—9	—3.3	26	16	60.8	35	95	54	129.2
—22.2	—8	—3	26.6	16.1	61	35.5	96	54.4	130
—22	—7.6	—2.7	27	16.6	62	36	96.8	55	131
—21.6	—7	—2.2	28	17	62.6	36.1	97	55.5	132
—21.1	—6	—2	28.4	17.2	63	36.6	98	56	132.8
—21	—5.8	—1.6	29	17.7	64	37	98.6	56.1	133

THERMOMETRIC EQUIVALENTS.—(*Continued.*)

C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°
56.6	134	77.2	171	98	208.4	118.8	246	139.4	283
57	134.6	77.7	172	98.3	209	119	246.2	140	284
57.2	135	78	172.4	98.8	210	119.4	247	140.5	285
57.7	136	78.3	173	99	210.2	120	248	141	285.8
58	136.4	78.8	174	99.4	211	120.5	249	141.1	286
58.3	137	79	174.2	100	212	121	249.8	141.6	287
58.8	138	79.4	175	100.5	213	121.1	250	142	287.6
59	138.2	80	176	101	213.8	121.6	251	142.2	288
59.4	139	80.5	177	101.1	214	122	251.6	142.7	289
60	140	81	177.8	101.6	215	122.2	252	143	289.4
60.5	141	81.1	178	102	215.6	122.7	253	143.3	290
61	141.8	81.6	179	102.2	216	123	253.4	143.8	291
61.1	142	82	179.6	102.7	217	123.3	254	144	291.2
61.6	143	82.2	180	103	217.4	123.8	255	144.4	292
62	143.6	82.7	181	103.3	218	124	255.2	145	293
62.2	144	83	181.4	103.8	219	124.4	256	145.5	294
62.7	145	83.3	182	104	219.2	125	257	146	294.8
63	145.4	83.8	183	104.4	220	125.5	258	146.1	295
63.3	146	84	183.2	105	221	126	258.8	146.6	296
63.8	147	84.4	184	105.5	222	126.1	259	147	206.6
64	147.2	85	185	106	222.8	126.6	260	147.2	297
64.4	148	85.5	186	106.1	223	127	260.6	147.7	298
65	149	86	186.8	106.6	224	127.2	261	148	298.4
65.5	150	86.1	187	107	224.6	127.7	262	148.3	299
66	150.8	86.6	188	107.2	225	128	262.4	148.8	300
66.1	151	87	188.6	107.7	226	128.3	263	149	300.2
66.6	152	87.2	189	108	226.4	128.8	264	149.4	301
67	152.6	87.7	190	108.3	227	129	264.2	150	302
67.2	153	88	190.4	108.8	228	129.4	265	150.5	303
67.7	154	88.3	191	109	228.2	130	266	151	303.8
68	154.4	88.8	192	109.4	229	130.5	267	151.1	304
68.3	155	89	192.2	110	230	131	267.8	151.6	305
68.8	156	89.4	193	110.5	231	131.1	268	152	305.6
69	156.2	90	194	111	231.8	131.6	269	152.2	306
69.4	157	90.5	195	111.1	232	132	269.6	152.7	307
70	158	91	195.8	111.6	233	132.2	270	153	307.4
70.5	159	91.1	196	112	233.6	132.7	271	153.3	308
71	159.8	91.6	197	112.2	234	133	271.4	153.8	309
71.1	160	92	197.6	112.7	235	133.3	272	154	309.2
71.6	161	92.2	198	113	235.4	133.8	273	154.4	310
72	161.6	92.7	199	113.3	236	134	273.2	155	311
72.2	162	93	199.4	113.8	237	134.4	274	155.5	312
72.7	163	93.3	200	114	237.2	135	275	156	312.8
73	163.4	93.8	201	114.4	238	135.5	276	156.1	313
73.3	164	94	201.2	115	239	136	276.8	156.6	314
73.8	165	94.4	202	115.5	240	136.1	277	157	314.6
74	165.2	95	203	116	240.8	136.6	278	157.2	315
74.4	166	95.5	204	116.1	241	137	278.6	157.7	316
75	167	96	204.8	116.6	242	137.2	279	158	316.4
75.5	168	96.1	205	117	242.6	137.7	280	158.3	317
76	168.8	96.6	206	117.2	243	138	280.4	158.8	318
76.1	169	97	206.6	117.7	244	138.3	281	159	318.2
76.6	170	97.2	207	118	244.4	138.8	282	159.4	319
77	170.6	97.7	208	118.3	245	139	282.2	160	320

THERMOMETRIC EQUIVALENTS.—(*Continued.*)

C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°
160.5	321	181.1	358	202	395.6	222.7	433	243.3	470
161	321.8	181.6	359	202.2	396	223	433.4	243.8	471
161.1	322	182	359.6	202.7	397	223.3	434	244	471 2
161.6	323	182.2	360	203	397.4	223.8	435	244.4	472
162	323.6	182.7	361	203.3	398	224	435.2	245	473
162.2	324	183	361.4	203 8	399	224.4	436	245.5	474
162.7	325	183.3	362	204	399.2	225	437	246	474.8
163	325.4	183.8	363	204.4	400	225 5	438	246.1	475
163.3	326	184	363.2	205	401	226	438.8	246.6	476
163.8	327	184.4	364	205.5	402	226.1	439	247	476.6
164	327.2	185	365	206	402.8	226.6	440	247.2	477
164.4	328	185.5	366	206.1	403	227	440.6	247.7	478
165	329	186	366.8	206.6	404	227.2	441	248	478.4
165.5	330	186.1	367	207	404.6	227.7	442	248 3	479
166	330.8	186.6	368	207.2	405	228	442.4	248.8	480
166.1	331	187	368.6	207.7	406	228.3	443	249	480.2
166.6	332	187.2	369	208	406.4	228.8	444	249.4	481
167	332.6	187.7	370	208.3	407	229	444.2	250	482
167.2	333	188	370.4	208.8	408	229.4	445	250.5	483
167.7	334	188.3	371	209	408.2	230	446	251	483.8
168	334.4	188.8	372	209.4	409	230.5	447	251.1	484
168.3	335	189	372.2	210	410	231	447.8	251.6	485
168.8	336	189.4	373	210.5	411	231.1	448	252	485.6
169	336.2	190	374	211	411.8	231.6	449	252.2	486
169.4	337	190.5	375	211.1	412	232	449.6	252.7	487
170	338	191	375.8	211.6	413	232.2	450	253	487.4
170.5	339	191.1	376	212	413.6	232.7	451	253.3	488
171	339.8	191.6	377	212.2	414	233	451.4	253.8	489
171.1	340	192	377.6	212.7	415	233.3	452	254	489.2
171.6	341	192.2	378	213	415.4	233.8	453	254.4	490
172	341.6	192.7	379	213.3	416	234	453.2	255	491
172.2	342	193	379.4	213.8	417	234.4	454	255.5	492
172.7	343	193.3	380	214	417.2	235	455	256	492.8
173	343.4	193.8	381	214.4	418	235.5	456	256.1	493
173.3	344	194	381.2	215	419	236	456.8	256.6	494
173.8	345	194.4	382	215.5	420	236.1	457	257	494.6
174	345.2	195	383	216	420.8	236.6	458	257.2	495
174.4	346	195 5	384	216.1	421	237	458.6	257.7	496
175	347	196	384.8	216.6	422	237.2	459	258	496.4
175.5	348	196.1	385	217	422.6	237.7	460	258.3	497
176	348.8	196.6	386	217.2	423	238	460.4	258.8	498
176.1	349	197	386.6	217.7	424	238.3	461	259	498.2
176.6	350	197.2	387	218	424.4	238.8	462	259.4	499
177	350.6	197.7	388	218.3	425	239	462.2	260	500
177.2	351	198	388.4	218.8	426	239.4	463	260.5	501
177.7	352	198.3	389	219	426.2	240	464	261	501.8
178	352.4	198.8	390	219.4	427	240.5	465	261.1	502
178.3	353	199	390.2	220	428	241	465.8	261.6	503
178.8	354	199.4	391	220.5	429	241.1	466	262	503.6
179	354.2	200	392	221	429.8	241.6	467	262.2	504
179.4	355	200.5	393	221.1	430	242	467.6	262.7	505
180	356	201	393.8	221.6	431	242.2	468	263	505.4
180.5	357	201.1	394	222	431.6	242.7	469	263.3	506
181	357.8	201.6	395	222.2	432	243	469.4	263.8	507

THERMOMETRIC EQUIVALENTS.—(*Continued.*)

C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°
264	507.2	271.6	521	278.8	534	286.1	547	293.3	560
264.4	508	272	521.6	279	534.2	286.6	548	293.8	561
265	509	272.2	522	279.4	535	287	548.6	294	561.2
265.5	510	272.7	523	280	536	287.2	549	294.4	562
266	510.8	273	523.4	280.5	537	287.7	550	295	563
266.1	511	273.3	524	281	537.8	288	550.4	295.5	564
266.6	512	273.8	525	281.1	538	288.3	551	296	564.8
267	512.6	274	525.2	281.6	539	288.8	552	296.1	565
267.2	513	274.4	526	282	539.6	289	552.2	296.6	566
267.7	514	275	527	282.2	540	289.4	553	297	566.6
268	514.4	275.5	528	282.7	541	290	554	297.2	567
268.3	515	276	528.8	283	541.4	290.5	555	297.7	568
268.8	516	276.1	529	283.3	542	291	555.8	298	568.4
269	516.2	276.6	530	283.8	543	291.1	556	298.3	569
269.4	517	277	530.6	284	543.2	291.6	557	298.8	570
270	518	277.2	531	284.4	544	292	557.6	299	570.2
270.5	519	277.7	532	285	545	292.2	558	299.4	571
271	519.8	278	532.4	285.5	546	292.7	559	300	572
271.1	520	278.3	533	286	546.8	293	559.1		

SPECIFIC GRAVITY TABLES.

Beaumé's Scale for Liquids Lighter than Water.

The following table is calculated for a temperature of 17.5° C. (63.5° F.), and is based on the formulas $\frac{140}{B.^\circ + 130}$ = specific gravity and $\frac{140}{\text{specific gravity}} - 130 = B.^\circ$

Degree Baumé.	Specific Gravity.	Degree Baumé.	Specific Gravity.	Degree Baumé.	Specific Gravity.	Degree Baumé.	Specific Gravity.
10	1.0000	33	0.8588	56	0.7526	79	0.6698
11	0.9929	34	0.8536	57	0.7486	80	0.6666
12	0.9859	35	0.8484	58	0.7446	81	0.6635
13	0.9790	36	0.8433	59	0.7407	82	0.6604
14	0.9722	37	0.8383	60	0.7368	83	0.6573
15	0.9655	38	0.8333	61	0.7329	84	0.6542
16	0.9589	39	0.8284	62	0.7290	85	0.6511
17	0.9523	40	0.8235	63	0.7253	86	0.6482
18	0.9459	41	0.8187	64	0.7216	87	0.6452
19	0.9395	42	0.8139	65	0.7179	88	0.6422
20	0.9333	43	0.8092	66	0.7142	89	0.6393
21	0.9271	44	0.8045	67	0.7106	90	0.6363
22	0.9210	45	0.8000	68	0.7070	91	0.6335
23	0.9150	46	0.7954	69	0.7035	92	0.6306
24	0.9090	47	0.7909	70	0.7000	93	0.6278
25	0.9032	48	0.7865	71	0.6965	94	0.6250
26	0.8974	49	0.7821	72	0.6931	95	0.6222
27	0.8917	50	0.7777	73	0.6896	96	0.6195
28	0.8860	51	0.7734	74	0.6863	97	0.6167
29	0.8805	52	0.7692	75	0.6829	98	0.6140
30	0.8750	53	0.7650	76	0.6796	99	0.6113
31	0.8695	54	0.7608	77	0.6763	100	0.6087
32	0.8641	55	0.7567	78	0.6731		

Baumé's Scale for Liquids Heavier than Water.

Degrees.	Baumé, 17.5° C.	Rational Baumé Scale, 12.5° C.	Degrees.	Baume, 17.5° C.	Rational Baumé Scale, 12 5° C.
	Sp. gr.	Sp. gr.		Sp. gr.	Sp. gr.
0	1.0000	1.0000	37	1.3370	1.3447
1	1.0068	1.0069	38	1.3494	1.3574
2	1.0138	1.0140	39	1.3619	1.3703
3	1.0208	1.0212	40	1.3746	1.3834
4	1.0280	1.0285	41	1.3876	1.3968
5	1.0353	1.0358	42	1.4009	1.4105
6	1.0426	1.0434	43	1.4143	1.4244
7	1.0501	1.0509	44	1.4281	1.4386
8	1.0576	1.0587	45	1.4421	1.4531
9	1.0653	1.0665	46	1.4564	1.4678
10	1.0731	1.0745	47	1.4710	1.4828
11	1.0810	1.0825	48	1.4860	1.4984
12	1.0890	1.0907	49	1.5012	1.5141
13	1.0972	1.0990	50	1.5167	1.5301
14	1.1054	1.1074	51	1.5325	1.5466
15	1.1138	1.1160	52	1.5487	1.5633
16	1.1224	1.1247	53	1.5652	1.5804
17	1.1310	1.1335	54	1.5820	1.5978
18	1.1398	1.1425	55	1.5993	1.6158
19	1.1487	1.1516	56	1.6169	1.6342
20	1.1578	1.1608	57	1.6349	1.6529
21	1.1670	1.1702	58	1.6533	1.6720
22	1.1763	1.1798	59	1.6721	1.6916
23	1.1858	1.1896	60	1.6914	1.7116
24	1.1955	1.1994	61	1.7111	1.7322
25	1.2053	1.2095	62	1.7313	1.7532
26	1.2153	1.2198	63	1.7520	1.7748
27	1.2254	1.2301	64	1.7731	1.7960
28	1.2357	1.2407	65	1.7948	1.8195
29	1.2462	1.2515	66	1.8171	1.8428
30	1.2569	1.2624	67	1.8398	1.839
31	1.2677	1.2736	68	1.8632	1.864
32	1.2788	1.2849	69	1.8871	1.885
33	1.2901	1.2965	70	1.9117	1.909
34	1.3015	1.3082	71	1.9370	1.935
35	1.3131	1.3202	72	1.9629	1.960
36	1.3250	1.3324			

What is known as the "Rational" Baumé scale is calculated by taking water at the temperature chosen at 0° B. and sulphuric acid of 1.842 specific gravity at 66° B. and using the formula $\frac{144.3}{144.3 - n^\circ} = d$. (See Lunge's "Sulphuric Acid and Alkali," Vol. I. p. 20.)

Comparison of the Twaddle Scale with the Rational Baumé Scale.

Twaddle.	Baumé.	Specific Gravity.	Twaddle.	Baumé.	Specific Gravity.	Twaddle.	Baumé.	Specific Gravity.	Twaddle.	Baumé.	Specific Gravity.
0	0	1.000	44	26.0	1.220	88	44.1	1.440	131	57.1	1.655
1	0.7	1.005	45	26.4	1.225	89	44.4	1.445	132	57.4	1.660
2	1.4	1.010	46	26.9	1.230	90	44.8	1.450	133	57.7	1.665
3	2.1	1.015	47	27.4	1.235	91	45.1	1.455	134	57.9	1.670
4	2.7	1.020	48	27.9	1.240	92	45.4	1.460	135	58.2	1.675
5	3.4	1.025	49	28.4	1.245	93	45.8	1.465	136	58.4	1.680
6	4.1	1.030	50	28.8	1.250	94	46.1	1.470	137	58.7	1.685
7	4.7	1.035	51	29.3	1.255	95	46.4	1.475	138	58.9	1.690
8	5.4	1.040	52	29.7	1.260	96	46.8	1.480	139	59.2	1.695
9	6.0	1.045	53	30.2	1.265	97	47.1	1.485	140	59.5	1.700
10	6.7	1.050	54	30.6	1.270	98	47.4	1.490	141	59.7	1.705
11	7.4	1.055	55	31.1	1.275	99	47.8	1.495	142	60.0	1.710
12	8.0	1.060	56	31.5	1.280	100	48.1	1.500	143	60.2	1.715
13	8.7	1.065	57	32.0	1.285	101	48.4	1.505	144	60.4	1.720
14	9.4	1.070	58	32.4	1.290	102	48.7	1.510	145	60.6	1.725
15	10.0	1.075	59	32.8	1.295	103	49.0	1.515	146	60.9	1.730
16	10.6	1.080	60	33.3	1.300	104	49.4	1.520	147	61.1	1.735
17	11.2	1.085	61	33.7	1.305	105	49.7	1.525	148	61.4	1.740
18	11.9	1.090	62	34.2	1.310	106	50.0	1.530	149	61.6	1.745
19	12.4	1.095	63	34.6	1.315	107	50.3	1.535	150	61.8	1.750
20	13.0	1.100	64	35.0	1.320	108	50.6	1.540	151	62.1	1.755
21	13.6	1.105	65	35.4	1.325	109	50.9	1.545	152	62.3	1.760
22	14.2	1.110	66	35.8	1.330	110	51.2	1.550	153	62.5	1.765
23	14.9	1.115	67	36.2	1.335	111	51.5	1.555	154	62.8	1.770
24	15.4	1.120	68	36.6	1.340	112	51.8	1.560	155	63.0	1.775
25	16.0	1.125	69	37.0	1.345	113	52.1	1.565	156	63.2	1.780
26	16.5	1.130	70	37.4	1.350	114	52.4	1.570	157	63.5	1.785
27	17.1	1.135	71	37.8	1.355	115	52.7	1.575	158	63.7	1.790
28	17.7	1.140	72	38.2	1.360	116	53.0	1.580	159	64.0	1.795
29	18.3	1.145	73	38.6	1.365	117	53.3	1.585	160	64.2	1.800
30	18.8	1.150	74	39.0	1.370	118	53.6	1.590	161	64.4	1.805
31	19.3	1.155	75	39.4	1.375	119	53.9	1.595	162	64.6	1.810
32	19.8	1.160	76	39.8	1.380	120	54.1	1.600	163	64.8	1.815
33	20.3	1.165	77	40.1	1.385	121	54.4	1.605	164	65.0	1.820
34	20.9	1.170	78	40.5	1.390	122	54.7	1.610	165	65.2	1.825
35	21.4	1.175	79	40.8	1.395	123	55.0	1.615	166	65.5	1.830
36	22.0	1.180	80	41.2	1.400	124	55.2	1.620	167	65.7	1.835
37	22.5	1.185	81	41.6	1.405	125	55.5	1.625	168	65.9	1.840
38	23.0	1.190	82	42.0	1.410	126	55.8	1.630	169	66.1	1.845
39	23.5	1.195	83	42.3	1.415	127	56.0	1.635	170	66.3	1.850
40	24.0	1.200	84	42.7	1.420	128	56.3	1.640	171	66.5	1.855
41	24.5	1.205	85	43.1	1.425	129	56.6	1.645	172	66.7	1.860
42	25.0	1.210	86	43.4	1.430	130	56.9	1.650	173	67.0	1.865
43	25.5	1.215	87	43.8	1.435						

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